Functionalised poly(organosiloxane)s as supported liquid membranes

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FUNCTIONALISED POLY(ORGANOSILOXANE)S AS SUPPORTED LIQUID MEMBRANES

Submitted by **Michael Maxwell**

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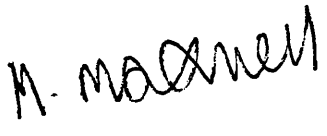

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I find it hard to believe I am writing the last page of my thesis (I guess I will not be the only one) so I would like to take this opportunity to thank the people who have made my time in Bath so enjoyable. First off I would like to thank the guys in 2.10 Chris, Jo, Phil, Dave, Sean, Mike, John and Tim who all know how to work and how to have fun. I would like to thank 2.29 (Chini, Richard and Susanna) for putting up with me. I would like to thank Tim and Jim for their support when I was writing up even if this was only so their could get hold of my office and computer. I would like to thank Ed for not knowing the difference between 3 months and 2 years. My first year in Bath was made easy to settle into by a good group of friends who have now left Bath but are not forgotten Marc, Carl, Mike, Alex , Jim, Sarah and Jo. I would also like to thank Wayne for the introduction to absinth and the Glastonbury gang for the few days of madness.

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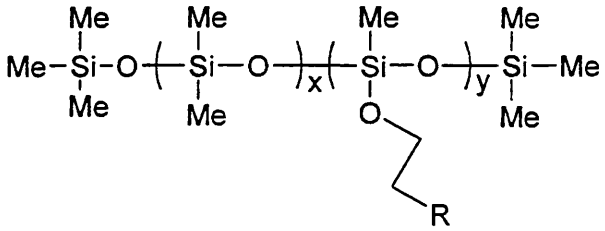
ABSTRACT

In this project fluid functionalised poly(organosiloxane)s were synthesised and used as SLMs for the transport of aqueous organic substrates; the mechanism(s) of the transport processes were also investigated. Studies centred on phenolic compounds, firstly because of their environmental significance, and secondly as convenient models for weak organic acids in general. Four classes of functionalised poly(organosiloxane) fluids were synthesised. These contained amine, ether, ester or methyl functionalities separated from the polymer chain by an alkyl spacer. Poly(organosiloxane)s were synthesised in high yields by a hydrogen elimination reaction between dimethylsiloxane-methylhydrosiloxane co-polymers and a primary alcohol in the presence of a platinum catalyst. The general formula of the functionalised poly(organosiloxane)s, each of which were prepared with different loadings (*ca* 4 %, 16 % and 30 mol %), is shown below;



R = CH_2NMe_2, OCH_2CH_3 , CH_2CH_3, $(CH_2)_3CO_2Et$

A small SLM test rig apparatus was built which had a membrane area of 1.59×10^{-3} m^2. It was used initially for batch experiments in which the aqueous phenol feed and the stripping phase were stirred and equilibrium attained before they were analysed quantitatively. The results showed that both amine and ether functionalised poly(organosiloxane) SLMs transport phenol against a concentration gradient if an alkaline stripping phase is used. Approximately 95% phenol extraction was possible at steady state with a stripping of 1.0M NaOH.

Continuous flow experiments were next carried out in order to gain an understanding of the transport mechanism. A facilitated transport mechanism was

demonstrated for both the amine and ether functionalised poly(organosiloxane) SLMs using a 0.1M NaOH stripping phase. The phenol facilitated flux increased from 15 to 62 ± 10 g/hour/m^{-2} as the amine functional loading group of the siloxane increased from 4 mol % to 30 mole %. In contrast phenol facilitated fluxes through ether functionalised poly(or]ganosiloxane)s SLMs at the same phenol phase concentration (3% w/w) did not increase with an increase in ether loading, but remained constant at *ca* 30 ± 10 g/hour/m^{-2} at all loadings investigated. Results for the phenol derivatives hydroquinone (pK_a 10.35) and methoxyphenol (pK_a 10.17) followed similar trends to those for phenol for both amine and ether functionalised poly(organosiloxane) SLMs. Thus slight changes in the acidity of the substrate appear to have little effect on the transport mechanism.

The working lifetimes of amine and ether functionalised poly(organosiloxane) SLMs are determined by the functional group loading and the substrate being transported. High functional group loadings and substrate fluxes destabilise the SLMs. The working lifetimes of the 4 mol % amine and ether functionalised SLMs for phenol transport are at *ca* 3 days comparable with those of amine carrier[87-90] and solvent only[80] flat sheet supported systems.

CONTENTS

Abbreviations

Å	Ångstrom
asym	Asymmetric
br	Broad
Bu	Butyl
COD	1,5-Cyclooctadiene
d	Doublet
DCM	Dichloromethane
ELM	Emulsion liquid membrane
Et	Ethyl
FT	Fourier transform
IR	Infra-red (spectroscopy)
m	Multiple
Mpt	Melting point
NMR	Nuclear magnetic resonance (spectroscopy)
Ph	Phenyl
ppm	Parts per million
q	Quartet
R	Alkyl
s	Singlet
SLM	Supported liquid membrane
sym	Symmetric
T_1	Spin-lattice relaxation time
t	Triplet
TMS	Tetramethylsilane

CHAPTER 1

INTRODUCTION

1.0 MEMBRANE TREATMENT OF AQUEOUS WASTE

New pollution control legislation and increased competition together have forced the chemical industry to take action to reduce the amount of chemical waste, in particular aqueous waste, produced in its manufacturing processes, and to search for more efficient ways of separating and utilising that which is formed. Traditional methods used in the recovery of a wide variety of chemicals include affinity adsorption chromatography[1], ion exchange[2], distillation[3] and solvent extraction[4]. These methods have inherent problems associated with their use, including the use of flammable and toxic solvents, the need to regenerate the solvents, high capital costs, and high energy consumption. Membrane processes have been investigated as an alternative approach to waste treatment, as they might overcome the problems associated with more traditional methods. Membrane based processes which show promise include:

i) Filtration membranes[5-10]. In filtration the membrane separates by size exclusion, only allowing certain sized particles/molecules to pass through the membrane. Filtration membranes are divided into three main categories. These are:

a) Microfiltration.
b) Ultrafiltration.
c) Nanofiltration.

The three main types of filtration membrane differ according to the particle size that each of the membranes can filter (see table 1.1). Each of the three types of membranes can be utilised for pollution control.

Micro[5] and ultrafiltration[6,7] membranes are porous membranes used to separate particles/ macromolecules, including proteins in solution. Microfiltration membranes have larger pores, up to 20 microns diameter. Ultrafiltration membranes have pore sizes between 1 and 20 nm. The driving force used for separation is usually pressure, with greater pressure being applied to the smaller pore size membranes. Values for

microfiltration processes are typically 50-100 kPa, and those for ultrafiltration are generally between 100-1000 kPa.

Nanofiltration[8,9] membranes contain no conventional pores. These consist typically of asymmetric polymeric films through which the substrate diffuses. The asymmetric nature of the polymer leads to small irregular gaps which provides channels through which the substrate travels. In this way small molecular weight substrates of between 300 and 1000 Daltons can pass through the membrane, which provides a technique by which moderately sized organic compounds can be separated from smaller species. Typical pressures applied to nanofiltration membranes are 1,000 to 10,000 kPa.

ii) Dialysis[11-15]. In dialysis the driving force is an activity difference of the solute on each side of the membrane. Dialysis membranes selectively allow low-molecular weight molecular solutes to pass through, and reject large colloidal and high molecular-weight solutes (see table 1.1). Dialysis membranes are used mainly to separate salts and microsolutes from macromolecular solutions, as occurs in artificial kidneys. Other applications include purification of bio-products or alcohol reduction in beer.

Electrodialysis[14,15] is one important form of dialysis in which the activity difference driving force is created by an electrical potential gradient across the membrane. Ion-exchange membranes are used in conjunction with an electric field to selectively remove ionic species by alternately stacking cationic and anionic ion-exchange membranes. The most important large-scale application of electrodialysis is the production of drinking water from brackish water[14]. Other applications involve the removal of salts from pharmaceutical solutions and for the production of salt from sea water[15].

iii). *Pervaporation*[16-20] This process utilises the differing permeabilities of components of a mixture through a dense membrane in order to separate the components. Permeability is a function of both the solubility and the diffusivity coefficients (equation 1.1) of the substrate through a semi-permeable barrier. The ideal membrane material

will generally have a high permeability for the component that is to be separated, but a very low permeability for the other components of the mixture. The driving force for pervaporation is partial pressure difference of the substrate across the membrane (see table 1.1). This is generally maintained by creating a partial vacuum on the permeate side which is below the vapour pressure of the component to be separated, so that on reaching the permeate side that component vaporises. The name pervaporation arises from the combination of the terms permeation and evaporation.

$$P = D \times S \qquad \text{Equation 1.1}$$

P = Permeability coefficient.

D = Diffusivity coefficient.

S = Solubility coefficient.

The only current commercial use of pervaporation involves the dehydration of alcohols to break the azeotropic barrier[16], but a great deal of research is being carried out on the separation of organics from aqueous media[17,20]. The two most investigated membrane materials for organic separations in aqueous media are based on polyimides[17,18] and polysiloxanes[19,20]. Both polymers are highly hydrophobic so will have very low water permeability, but they can be chemically modified to achieve high organic permeability. A major drawback to pervaporation based separations is that different pervaporation membranes are needed for different separations.

Membrane separation process.	Driving force for mass transported.	Type of membrane employed.	Separation mechanism.	Preferably permeating component.	Application.
Micro-filtration	Hydrostatic pressure difference, 50-100kPa.	Symmetric macroporous membrane with a pore radius of 0.1-20	Sieving effect.	Continuos phase (solution).	Separation of suspensions and emulsions, sterile, particle free solution.
Ultra-filtration	Hydrostatic pressure difference, 100-1000kPa.	Symmetric mesoporous membrane with a pore radius of 1-20nm	Sieving effect	Micro-solution solution/solut ion of smaller macrosolute (solvent).	Concentration fractionation and macromolecul ar solutions, emulsions.
Nano-filtration	Hydrostatic pressure difference, 1000-10,000kPa.	Asymmetric membrane from differnce homogeneous polymers.	Solubility & diffusion in the homogeneous polymer matrix	Solvent	Concentration of components with low molecular weight.
Dialysis	Activity or concentration difference.	Symmetric mesoporous membrane.	Diffusion in a convection-free layer	Microsolute (ions).	Separation of components with low molecular weight from macromolecul ar solution.
Electro-dialysis	Difference in electrical potential.	Ion exchange membrane	Different charges of the component in solution	Microsolute (ions)	Desalting and De-acidifying of solution with neutral components.
Gas separation	Partial pressure difference, 10,000-15,000kPa.	Asymmetric membrane from homogeneous polymer.	Solution & diffusion in the homogeneous polymer matrix	All	Purification of gases
Pervaporation	Partial pressure difference.	Asymmetric solubility membrane from a homogeneous polymer	Solution & diffusion in the homogeneous polymer matrix	All.	Separation of low molecular weight organics
Liquid membranes	Concentration difference.	Liquid membrane.	Carrier and solvent.	All.	Separation of low molecular weight organics/ inorganics

Table 1.1 The main membrane processes and their applications.

1.1 MEMBRANE TRANSPORT PROCESSES

A membrane is a semi-permeable barrier between two phases, which can restrict the movement of solutes between these phases in a very specific manner. The two basic requirements for a membrane are that it acts as a barrier preventing intimate contact of the two phases, and that it is semi-permeable ensuring that selective transportation can be achieved.

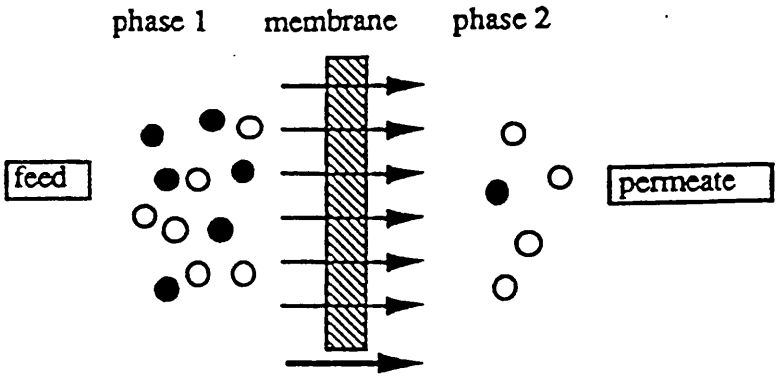


Figure 1.1 A typical membrane separation.

There are essentially three chemical/ physical properties of the components of a mixture which allow a membrane to retain or selectively transport that component. They are:

i) Large differences in the size of the components of the mixture (sieve effect). Membrane processes which use this property are microfiltration[5], ultrafiltration[6] and dialysis[11].

ii) Differences in solubility and/or diffusivity of the components through the membrane materials (solution-diffusion mechanism). Membranes processes and operations which use this mechanism are gas permeation[21], liquid membranes[22] and pervaporation[16].

iii) Differences in the charges of the species to be separated (electrochemical effect) which is used in electrodialysis[15].

The flux of a species through a membrane is dependent upon one of the above chemical/ physical properties and it can be related to the concentration gradient applied across the membrane, by Fick's first law of diffusion (equation 1.2).

$$J = (D/l)\,\Delta C \qquad \text{Equation 1.2}$$

J = Steady state flux.

D = Diffusivity.

l = Thickness of membrane.

ΔC = Concentration difference of the solute species across the membrane.

This law implies that transport will cease once the concentration of the component being transported is the same on both sides of the membrane, as there is no longer a driving force. For this reason many membrane processes cannot operate against a concentration gradient. If a membrane process is to operate against a concentration gradient then a different driving force must be provided.

1.2 LIQUID MEMBRANES

As noted above, the two basic requirements of a membrane are that it can both selectively separate the components of a mixture and stop the two phases mixing. These requirements can be met by a liquid. A liquid membrane can serve as a very effective physical barrier between two liquid phases with which it is immiscible, as well as separating solutes by the difference in permeabilities of each solute within the membrane. A considerable amount of research has been carried out on the creation of effective liquid membranes[22], and of the various types of liquid membranes that have been developed supported liquid[23] and emulsion liquid membranes[24-27] are the most common.

Liquid membranes have aroused a great deal of interest because of their ability to transport solutes against a concentration gradient by using coupled or facilitated transport. In this process the substrate interacts with a carrier dissolved within the membrane liquid which facilitates the transport of the substrate across the membrane by forming a substrate/carrier complex. The substrate/carrier interaction frequently involves H-bonding, as illustrated in figure 1.2, where a basic amine carrier H-bonds to a organic acid substrate. Ion exchange carriers have also been used in supported liquid membranes (SLMs). These utilise ionic interactions. Quaternary amine salts[28] are the most prevalent type of carrier in which the substrate anion replaces the initial carrier counter ion at the membrane/feed phase interface. The ion-pair or complex diffuses through the membrane, and on reaching the stripping phase a de-complexation reaction takes place which releases the substrate into the stripping phase in a form which cannot re-complex with the carrier. In the case of carriers which interact through H-bonding this is usually effected by having the stripping phase at a pH at which the substrate/carrier complex is unstable. In the case of ion exchange carriers the stripping phase is an ionic salt solution which contains ions which form a stronger complex with the substrate than the carrier does, hence causing de-complexation. An important feature of facilitated transport is that the carrier is continuously regenerated in its free form within the membrane.

Complexation reaction at the membrane/feed phase interface

$$R_3N + RCO_2H \rightarrow R_3N^+H\text{----}^-O_2CR$$

De-complexation reaction at the membrane/stripping phase interface

$$R_3N^+H\text{-----}^-O_2CR + NaOH \rightarrow R_3N + RCO_2^-Na^+ + H_2O$$

Figure 1.2 Reaction of an amine carrier with an organic acid.

1.2.1 EMULSION LIQUID MEMBRANES (ELM)

An emulsion liquid membrane is comprised of two immiscible phases mixed with a surfactant to produce an emulsion, which has been dispersed into the feed solution. Mass transfer takes place between the feed solution and the centre of the emulsion through the outer layer of the emulsion, which acts as the selective membrane.

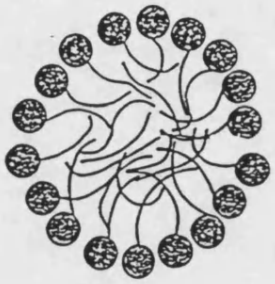


Figure 1.3 An oil/water emulsion stabilised by a surfactant.

In order to recover the substrate the emulsion phase is allowed to settle out and is then processed in order to regenerate the two immiscible layers. This is commonly accomplished by heating or centrifugation of the emulsion phase. The substrate is recovered from the phase which forms the inner layer of the emulsion.

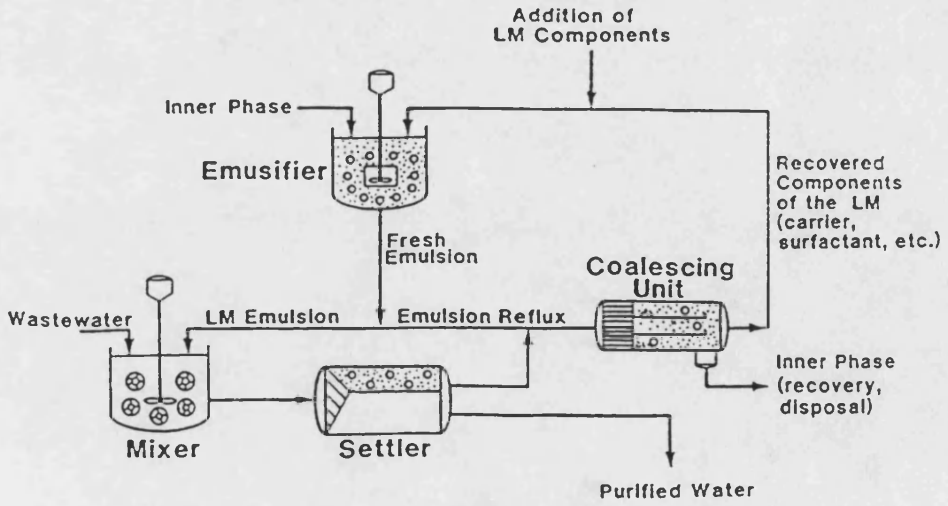


Figure 1.4 An ELM system.

Emulsion stability is a major problem associated with ELM based separations. The emulsion must be formulated to withstand the shear generated by mixing during extraction, but not so strong that it cannot be broken in order to release the internal phase. ELMs require a large number of processing steps thus making them an expensive option. Therefore their uses are limited to the recovery of expensive substrates which are difficult to isolate by any other technique[23-26].

A good example of this is provided by chiral separations which are generally difficult to achieve. Thus Chaudhuri[26] *et al* have shown that an ELM can be used to concentrate (D)-phenylalanine from a racemic mixture of (D/L)-phenylalanine. The ELM consisted of a copper(II)N-decyl-(L)-hydroxyproline complex in a hexanol:decane solvent. The copper complex is a chiral carrier which will form a complex with (D)-phenylalanine but not (L)-phenylalanine. The pH of the external phase of the emulsion hexanol/decane is kept at 4 but the internal phase has a pH of 6. At these pHs phenylalanine will concentrate in the external phase in the absence of complex formation. As only (D)-phenylalanine can react with the copper complex only one enantiomer will readily transfer to the internal phase. The concentration of (D)-phenylalanine relative to (L)-phenylalanine can be increased by a factor of 2.5 using this ELM system.

1.2.2 SUPPORTED LIQUID MEMBRANES (SLMs)

SLMs normally consist of an organic solvent (which may have an organic carrier dissolved within it) which is mobilised within a porous support. Flat polymer sheets with thicknesses ranging from 10 to 100 μm and with a pore size between 0.1 and 1μm are typically used as the support material in initial research investigations, but they have a small surface:volume ratio for practical purposes. Industrially, hollow fibre modules are used to provide a much larger surface area. The carrier is chosen to interact specifically with the substrate which is to be extracted. Carriers commonly used include crown ethers[29] and calixarenes[30] which can hydrogen bond to organic compounds including amino acids[90] as well as encapsulate inorganic metal[46-48] ions.

SLMs have many benefits over traditional methods for the recovery of specific chemicals:

i) Very selective separations are possible due to the selective nature of the carrier.

ii) Substrates can be transported against a concentration gradient.

iii) Only small amounts of carrier are required.

iv) There is a low energy requirement.

v) Only small amounts of solvent are required.

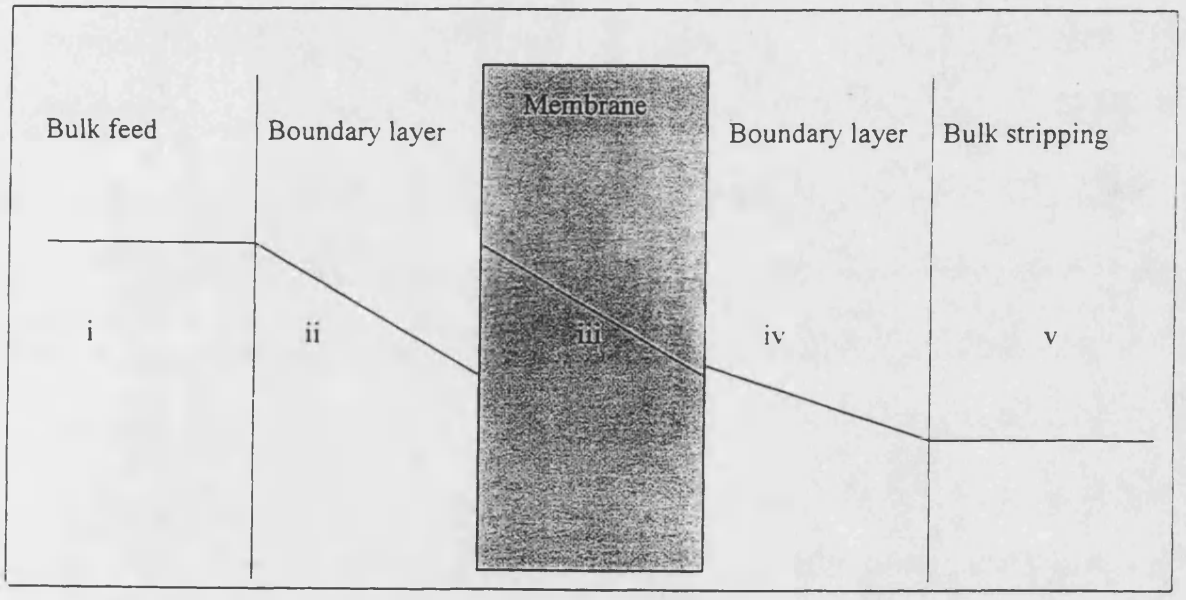
vi) SLMs can operate in the present of high salt concentration.

vii) Supported liquid membrane technology is very versatile.

1.2.3 TRANSPORTATION IN CARRIER ASSISTED SLMs

In order to transport a substrate against a concentration gradient a driving force is needed. One way to achieve this is to use a carrier assisted system with a pH gradient across the membrane.

The transport process for the substrate in a carrier assisted SLM can be divided into five discrete steps (figure 1.5);



i) Diffusion of the substrate through the boundary layer of the source phase.

ii) Complexation of the substrate with the carrier at the source/membrane interface.

iii) Diffusion of the substrate/carrier complex through the membrane.

iv) Release of the substrate at the membrane/receiving interface.

v) Diffusion of the substrate through the aqueous boundary layer of the receiving phase.

Figure 1.5 Concentration profile in a SLM.

In step one the substrate diffuses through the boundary layer formed when the concentration of the substrate at the source/membrane interface is reduced, due to the slower diffusion of the substrate from the bulk solution into the boundary layer compared to the faster transport of the substrate through the membrane (figure 1.6). A boundary layer effectively reduces the concentration gradient across the membrane hence reducing the flux. The thickness of the boundary layer can be reduced by increasing the degree of turbulence adjacent to the membrane, as this increases the diffusion rate of the substrate from the bulk phase into the boundary layer. It is worth noting that the membrane becomes fouled with the solutes overtime. The reason a layer of the solutes builds up on the membrane surface is due to the attractive electrostatic interactions between the solutes and the membrane.

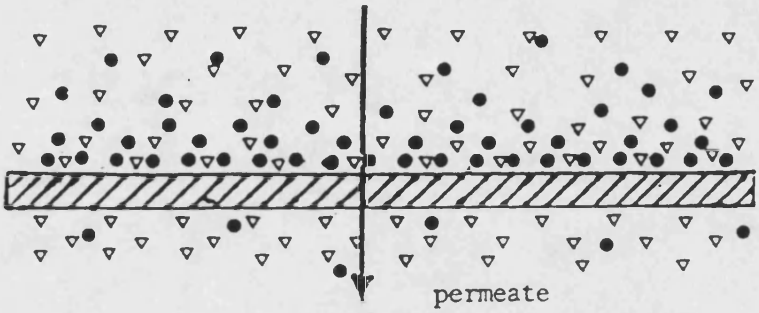


Figure 1.6 Boundary layer effect.

The second step in the transportation of the substrate is the formation of a complex between the carrier and the substrate at the interface of the membrane. The complex then diffuses though the membrane in response to the concentration gradient of the complex, with a high concentration of the complex at the feed phase /membrane interface but a lower concentration within the membrane.

When the complex reaches the stripping phase a de-complexation reaction takes place so liberating free substrate and carrier. This may be effected by having a different pH in the stripping phase to that in the feed phase. The carrier then diffuses back through the membrane, whilst the substrate diffuses through the stripping phase boundary layer and into the bulk stripping phase.

1.2.4 MODELLING TRANSPORT IN A SLM

In the simplest kind of SLM with the membrane pores containing only organic solvent, the species to be transported is distributed over the organic solvent phase and the bulk aqueous phase. The partition coefficient K_p of the substrate is defined as:

$$K_p = [S_o] / [S_a] \qquad \text{Equation 1.3}$$

S_o = Bulk concentration of substrate in organic membrane phase.
S_a= Bulk concentration of substrate in aqueous phase.

In equation 1.1 and 1.2 solubility and diffusivity are related to permeability which can in turn be related to flux. The solubility term in these equations can replaced by K_p to give equation 1.4.

$$J_s = K_p (D / L) (S_{af} - S_{as}). = K_p (D / L) \Delta S \qquad \text{Equation 1.4}$$

L = Membrane thickness.
D = Diffusivity of substrate in membrane phase.
J_s = Flux arising from the solubility of the substrate within the organic phase.
ΔS = Substrate concentration difference between feed and stripping phase (S_{af} - S_{as}).
Subscript f - feed side, S- stripping phase

In generally a SLM contains a carrier (C_o) that is able to form a complex (SC_o) with the substrate that is present within the organic phase (S_o). The equilibrium constant (K_e) for the formation of the complex (SC_o) is given by equation 1.5.

$$K_c = [SC_o] / [S_o][C_o] \qquad \text{Equation 1.5}$$

The flux for a carrier mediated system will equal the flux arising from the solubility of the substrate within the organic phase plus the flux due to the carrier (J_c)

$$J_{total} = J_s + J_c$$

$$J_{total} = [K_{p.}(D / L)] + [K_{e}.(D_{c.} / L)] \qquad \text{Equation 1.6}$$

J_{total} = Total overall flux.

D = Diffusivity of uncomplexed substrate.

D_c = Diffusivity of complexed substrate.

More detailed modelling by Reinhoult[29] *et al* have shown some common features of carrier assisted transport. These are:

i) The flux is proportional to the carrier concentration.

ii) The flux will show typical saturation behaviour. At low substrate concentration, flux is proportional to the substrate concentration, but at high substrate concentration flux is independent of substrate concentration.

iii) A strongly complexing carrier becomes fully loaded with substrate even for very low substrate concentrations, and therefore it does not produce a concentration gradient of the carrier/substrate complex over the membrane, as the de-complexation reaction is slow. This results in low fluxes.

1.3 APPLICATIONS OF SUPPORTED LIQUID MEMBRANES

The potential applications of supported liquid membranes can be divided into three discrete areas.

i) Separation of organics from aqueous media.
ii) Separation of inorganics from aqueous media.
iii) Analytical applications.

1.3.1 SEPARATION OF ORGANICS FROM AQUEOUS MEDIA

SLMs have aroused great interest for the separation of organics from aqueous waste streams as the techniques presently used for this purpose such as solvent extraction[4] and distillation[3] are both expensive and environmentally unfriendly. Organic acids[83-95] are the most investigated group of organic compounds and their separation by SLMs will be discussed in detail in section 1.6.

1.3.1.1 SEPARATION OF ORGANICS FROM FERMENTATION BROTHS

Fermentation is used to produce a large variety of organics, from lactic acid[31] to relatively high value pharmaceutical products such as penicillin[32,33]. Greater industrial use of fermentation has been impeded by its high cost, the large amount of energy needed in the separation step, and the low yield of product produced. For fermentation to be used more widely an improvement in the commonly used separation processes is needed. At the moment liquid-liquid extraction[32] is commonly used. This is not ideal as the solvent can be toxic to micro-organisms.

Membrane processes including dialysis[34], reverse osmosis[35] and pervaporation[36] have been investigated with some promising results, but they have not with very few exceptions been developed yet for industrial application. In the last few years a number

of studies[37-41] have been carried out using SLMs in coupled fermentation/separation bioreactors. The advantages of such a system is that continuous extraction is possible and the process is very energy efficient.

SLMs containing only long chain alcohols[40,41] have been used in the separation of aqueous butanol[40] and other alcohols[41]. The transport of the substrate alcohol is not facilitated as no carrier is present within the membrane, but it is driven by the high solubility of the alcohol substrate in the long chain alcohol of the SLM.

In the fermentation production of penicillin the separation of the product from the fermentation broth is very difficult due to the percursor phenylacetic acid (PPA) having similar chemical and physical properties to those of the product. In the SLM based separation of penicillin, tertiary amine (*e.g.* Amberline LA-2)[37,38] carriers are used in decanol solution. The amine H-bonds to the penicillin at pHs below 7, and it is transported to the stripping side which is maintained at a higher pH so causing de-complexation. Free PPA can also bind to an amine carrier, so in order to achieve the best separation of these two substances the feed and stripping phase pHs and the carrier concentration are varied. The best separation factor achieved for penicillin G[38] over PPA is 1.8, which is about the same as that achieved industrially using solvent extraction. The optimal conditions were found to be a feed phase pH of 6.0 to 6.5, a stripping phase of pH 7.0, and an amine carrier (Amberline LA-2) concentration greater than 200 mmol. The permeability of penicillin G at this conditions was 2.5×10^{-4} cm/s.

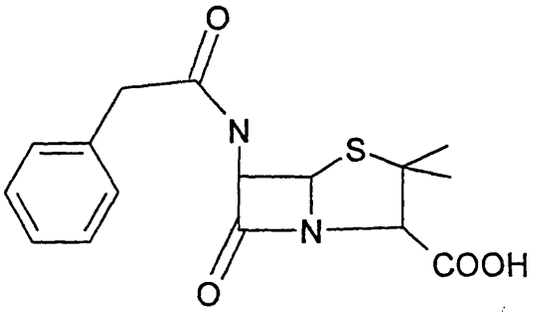


Figure 1.7 Penicillin G.

1.3.2 SEPARATION OF INORGANICS FROM AQUEOUS MEDIA

The separation of inorganic species can be divided into three main areas of interest. These are;

i) Separation of metal cations.

ii) Separation of inorganic anions.

iii) Separation of radioactive materials.

1.3.2.1 SEPARATION OF METAL CATIONS

The extraction of metal cations is one of the most studied areas of SLM activity[42-50]. Metals ions can pose major environmental problems. Thus a number of heavy metals appear on the red list[51] of chemical substances which cannot be discharged into the sewage system at any concentration. These metals such as Hg and Cd are currently removed by solvent extraction using amine extracts[52] and ion exchange[53].

As amines are very effective in solvent extraction they have also generated considerable interest as carriers in SLMs, with most studies concentrating on tri-octylamine[42-45] and dipyridyl derivatives[49] both of which have been studied for the extraction of a wide variety of metal cations ions. Neocuprine (figure 1.8) is a bidentate ligand which has also been used for the extraction of $Fe^{2+,3+}$ $Cu^{1+,2+}$ Cd^{2+} and Zn^{2+}. In batch runs with a feed phase metallic ion concentration of $1x\ 10^{-4}M$ complete extraction of Cu^{+}, Cd^{2+} ions, and 90% extraction of Zn^{2+}, was possible at steady state. With the other metals ions studied only *ca* 10% extraction was achieved at steady state under similar conditions.

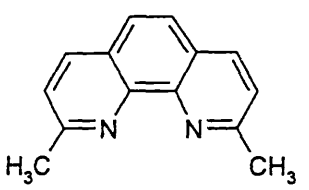


Figure 1.8 Neocuprine.

Crown ethers[47-48] are another group of compounds which have been studied as carriers. Crown ethers undergo substantial "bleeding" from the membrane phase into the aqueous phase because of their high aqueous solubility. This serious problem has been overcome by using mono-aza-crowns, instead of full oxo crowns, in the presence of an approximately equivalent amount of a long chain fatty acid[47]. The fatty acid and the aza-crown form an acid-base pair which has a much higher affinity for the organic phase than the simple crown.

Aza-18-crown-6 and palmitic acid[47] in chloroform SLMs have been investigated for the transportation of Cd^{2+}. The aza-crown forms a complex with Cd^{2+} which has a binding constant of $5x10^5$ M^{-1}. The stripping phase contains sodium thiosulphate (0.2 to 0.4M) which forms an even stronger complex with Cd^{2+} ions, so liberating the carrier. In batch runs with an aza-18-crown-6 concentration of $5x\ 10^{-5}$ M and a feed phase Cd^{2+} ion concentration of $3.6x\ 10^{-5}$ M complete extraction of Cd^{2+} was possible.

1.3.2.2 SEPARATION OF RADIOACTIVE METALS

The nuclear industry normally reprocesses the spent fuel from its power stations by solvent extraction. This process produces large amounts of active liquid waste which are reduced to a lower bulk by evaporation[54]. The non-active distillate is discharged into the environment and the concentrated liquid waste is kept in long-term storage. The evaporation step can only reduce the amount of liquid waste by a relatively small amount and it produces its own secondary waste.

To overcome these problems SLMs have been investigated[54-58] as an alternative procedure. Dicylohexane-18-crown-6[54,55] and crown-6-calix[4]arene[58] have been investigated as carriers for the selective separation of radioactive metals. These crowns have shown excellent results for the separation of radioactive strontium[85] and caesium[137] which are both β/γ emitters hence important isotopes to remove in reprocessing. In batch runs *ca* 90% extraction are possible for these two metal ions. Uranium(VI) ions have also been transported across a SLM with di(2-ethylhexyl)-

phosphoric acid[57] as a carrier and kerosene as the solvent. The highest uranium flux achieved was 1.45×10^{-6} mol/m^{-2}s^{-1}.

1.3.2.3 SEPARATION OF INORGANIC ANIONS

The transport of anions by SLMs has been barely reported[59-62] in comparison with cation transport. The anion transport systems are usually based on the use of macromolecules including crown ethers[59] and tetraphenylporphyrin (TTP)[62], into which a metal cation can be incorporated. The anion is transported via co-ordination to the metal centre which is in turn co-ordinated to the macromolecule.

Thus cyanide[62] ions have been transported using a TTP/Mn^{3+} complex as the carrier. The Mn^{3+} has a strong affinity for anionic ligands with especially strong affinities for CN^- ligands, this is illustrated by the equilibrium constant for the reaction between the two being 7×10^2 M^{-1} at pH 11.

$$Mn^{3+}(TPP)(OH^-) + CN^- \quad \leftrightarrow \quad Mn^{3+}(TPP)(CN^-) + OH^-$$

Facilitated transport is achieved by having a pH gradient across the membrane. The feed phase has a pH of 11 with the stripping phase having a pH of 14. This gives rise to a chemical potential difference with the formation of the CN^- complex being more favoured on the feed side than the stripping side, and vice versa for the OH^- complex. This causes the CN^- ion to undergo facilitated transport across the membrane.

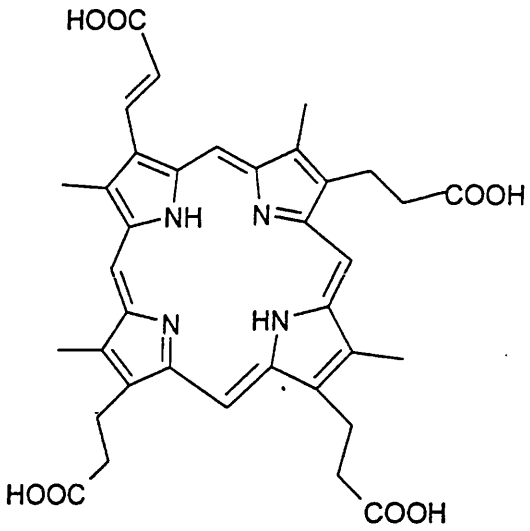


Figure 1.9 Porphyrin ring.

Very low fluxes are the main problem associated with the SLMs transportation of anions. Nakamura[62] *et al* estimated that the flux for CN^- transport using TTP/Mn^{2+} as the carrier was only 12% of the theoretical flux. These low fluxes are due to the slow diffusivity of the complex through the membrane due to the large size of the complexes formed.

1.3.3 PRE-TREATMENT STEP FOR ANALYTICAL DETERMINATIONS

The levels of most pesticides and herbicides in drinking water and in surface water are tightly controlled within the European Community at 0.1 and 1.0 μg/l respectively[63]. For determinations at such low concentrations a sample pre-treatment step is essential. For pesticide determinations in water samples liquid-liquid extraction is commonly used for this pre-treatment step. This procedure uses large volumes of organic solvents (often chlorinated) which makes this technique unattractive. Studies have been carried out using SLMs which contain only solvent within the membrane pores as an alternative to liquid-liquid extraction for pesticide and herbicide pre-concentration processes. A pH gradient is applied across the membrane with the stripping phase having a pH of *ca* 14. These studies showed that the extraction of ionisable herbicides and pesticides such as sulfonylurea[64-67] was more selective than the solvent extraction techniques. This type of SLM is not suitable for non-ionisable

pesticides and herbicides as they contain no carrier and depend upon the effect of the pH gradient to generate uncharged species in the feed and charged species in the stripping phase.

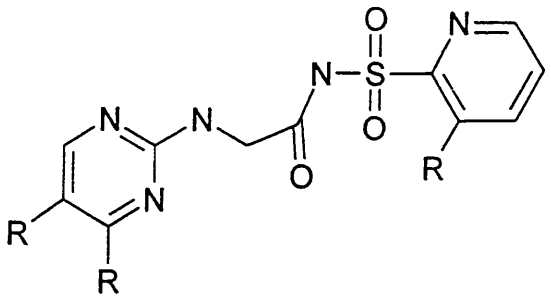


Figure 1.10 Sulfonylurea

Biological determinations such as drug levels in blood[68-69] involving the use of SLMs have generated considerable interest. Biological samples are acknowledged to be difficult to analyse due to their complexity, high salt concentration and low concentration of the substrate of interest. SLMs have been used to carry out pre-treatment of biological samples for the determination of basic drugs such as bambuterol[68], shown in figure 1.11.

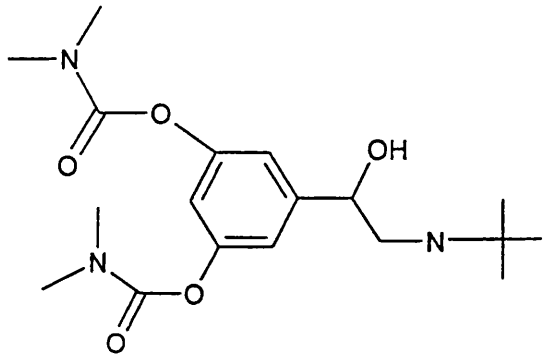


Figure 1.11 Bambuterol.

The SLMs used in these analytical determinations are carrier free and the separation is achieved by having a pH differential across the membrane. The feed side has a high pH and as bambuterol is an amine it is uncharged in the feed side. The stripping phase has a pH of 3.4 which will protonate the bambuterol and as charged species are not easily transported through the membrane, bambuterol is held in the

stripping phase. SLMs have been shown to be highly selective and more flexible than liquid-liquid extraction, which cannot be miniaturised and automated[69].

1.4 STABILITY OF SLMs

Industrial applications of SLM techniques are very limited because of concerns over the long term stability of SLMs. Membrane failure can occur in two ways. The first involves the loss of the carrier and occasionally solvent, to the aqueous medium. The loss of carrier results in the solute flux declining with time. The second form of instability results from penetration of the membrane by water, which finally causes direct channelling of the aqueous solution between feed and stripping side, and consequent failure of the membrane.

Before industrial applications can be seriously considered the stability of SLMs has to be improved. Research[70-76] into the process of SLM breakdown has shown that there are several mechanisms by which the membrane liquid can be lost and water penetration can occur. These can be summarised as:

i) Osmotic pressure mechanism.
ii) Progressive wetting mechanism.
iii) Pore-block mechanism.
iv) Shear-induced emulsion mechanism.

None of the mechanistic information so far accrued can fully answer the question of how and why a particular membrane becomes unstable.

1.4.1 OSMOTIC PRESSURE PROCESS

Osmotic pressure has been suggested by Chiarizia *et al*[70], Deblay *et al*[71] and Dozol *et al*[72] to have a major influence on SLM instability. The loss of membrane liquid in this process is caused by the osmotic pressure difference between the feed and stripping sides due to different ionic strengths on the two sides. This osmotic pressure driving force causes water transport through the membrane, and the lifetime of the SLM can be directly related to the water content in the membrane.

The importance of an osmotic pressure differential in causing SLM breakdown has been queried by Neplenbrock[73] *et al*. In some cases increasing the salt concentration in the aqueous feed phase, so increasing the osmotic pressure, reduces solvent removal from the SLM thus helping membrane stability. These authors suggest that water transport is a consequence of SLM instability and not the cause of SLM instability.

1.4.2 PROGRESSIVE WETTING PROCESS

In this process, first proposed by Takeuchi[74] *et al*, the interfacial tension forces keeping the solvent and carrier in the pores decrease over time so causing the membrane to fail. The interfacial tension decrease arises from the formation of a layer of contamination at the interface. When the interfacial tension decreases to a certain level, spontaneous emulsification takes place, so causing liquid loss from the membrane to the aqueous phase. In this circumstance the fluid lost to the aqueous phase would have the same composition as the membrane liquid within the pores. This is not observed to be the case in all examples of SLM instability, indicating that this is not the only process involved in SLM breakdown.

1.4.3 PORE-BLOCK PROCESS

This process was first considered by Babcock[75] *et al*. The pore-block process involves the formation of micelles. The micelles contain water on the inside with an organic carrier/substrate complex on the outside. As the micelles diffuse into the membrane interior they break up due to the complex concentration decreasing, and so liberate water. The water then coalesces into droplets and causes blockages in the pores. This results in the flux declining and expulsion of the membrane liquid into the adjacent aqueous phase. This process alone fails to explain why the ratio of the carrier to solvent in the liquid lost to the aqueous phase, differs from that in the membrane.

1.4.4 SHEAR-INDUCED EMULSION PROCESS

Fane[76] *et al* noted that the more stable an emulsion the organic carrier forms in water, the more unstable is the SLM impregnated with that organic carrier. From this observation he proposed a mechanism for SLM instability in which emulsion droplets are formed at the membrane/aqueous phase interface. These droplets are lost to the aqueous phase due to vibration or small pressure differences over the SLM. Thus the meniscus of the membrane liquid will withdraw into the pores and water will fill the vacated space. The process repeats itself as shown schematically in figure 1.12, until the membrane fails.

As is apparent from the above processes, many factors determine the stability of an SLM and more than one destabilising process can be operative at any one time. Further detailed research is needed to determine the exact relationship between SLM stability, composition and application.

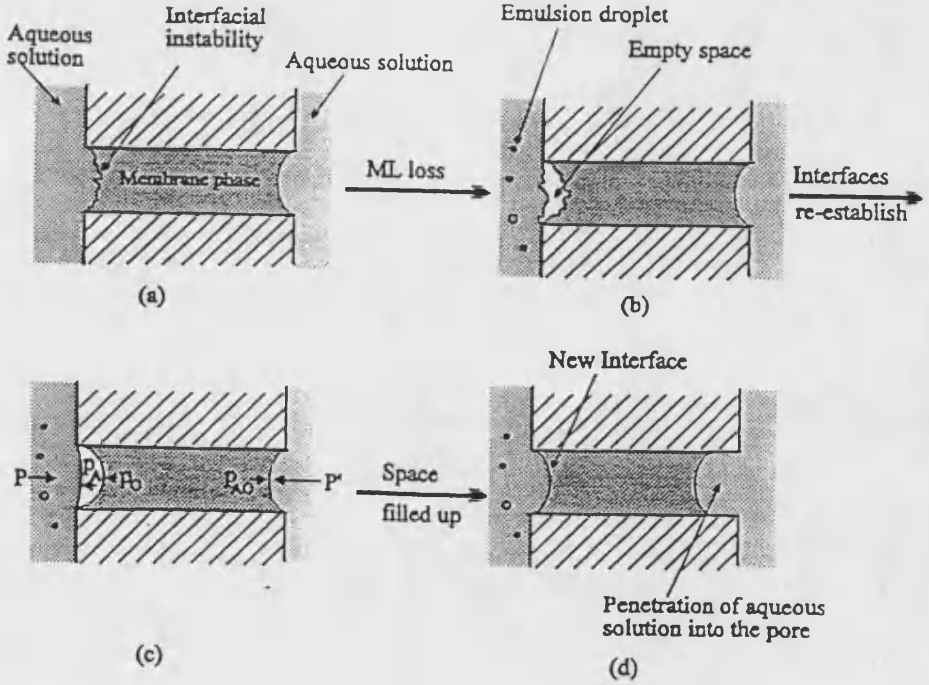


Figure 1.12 Shear-induced emulsion mechanism for membrane liquid loss.

1.5 PHENOL AS A MODEL SUBSTRATE FOR SLM SEPARATIONS

In this thesis a study of the transport of phenol and its derivatives through siloxane based SLMs is reported. Phenol was chosen for two reasons. Firstly it is an important industry compound as noted in 1.5.1, but it also creates a severe water contamination problem. Consequently a cheap and effective method for the removal of low concentrations of phenol from aqueous streams would be of significant value. The second reason for choosing phenol is that it can be used as a model for SLM mediated transport of other weakly acidic organic compounds. Unlike the majority of non-aromatic organic acids phenol can be determined quantitatively with ease *via* UV spectrophotometry.

1.5.1 PHENOL

Most phenol produced commercially is used in the formation of caprolactam, adipic acid, aniline and phenol-formaldehyde resins. These products all have significant economic importance and are used for the production of a wide range of consumer goods and process materials. The estimated world-wide production of phenol for 1990 was 5.0×10^6 tonnes[77].

The vast majority of phenol is produced by either cumene oxidation or by toluene oxidation[78]. The former process is often the most economic as acetone is produced as a valuable by-product . One significant disadvantage of the cumene oxidation process is that waste water containing 1-3% phenol is produced. Due to the high toxicity of phenol, its concentration must be reduced significantly before it can be discharged into sewage systems. The most commonly used method of removing phenol from aqueous streams is by liquid-liquid extraction, using either cumene or acetophenone as extractant, both of which are produced during the manufacturing process. The phenol concentration is typically reduced to 20-500 ppm by this treatment before being passed to the biological purification stage in a sewage treatment plant.

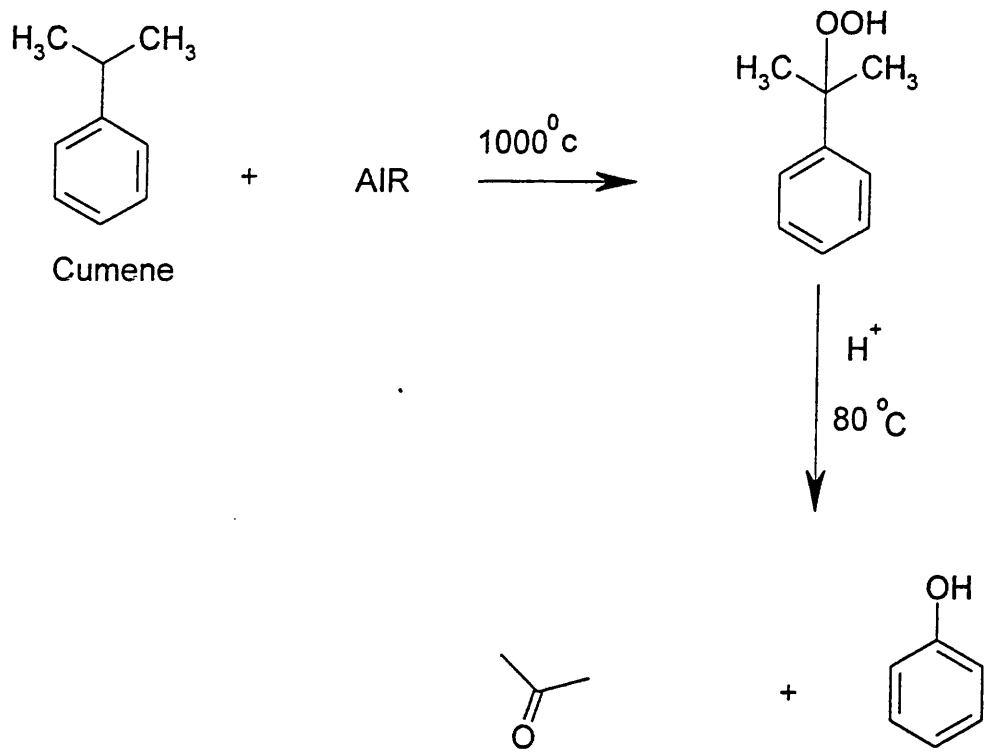


Figure 1.13 Cumene oxidation

Phenol waste-water streams are also produced in phenolic resin production and in the coking of coal. The concentration of phenol can be as high as 10% initially in the resultant wastewater streams[79].

Phenol is acutely toxic, affecting the central nervous system with the main absorption route being through the skin. The limiting concentration in the air for occupation health laid down for workers protection in the USA is 5 ppm.

1.6 SLM EXTRACTION OF AQUEOUS PHENOL

Three types of SLMs have been explored previously[80-92] for the extraction of aqueous phenol. Each is driven by a different transport mechanism as shown below.

1.6.1 EXTRACTION OF PHENOL USING ION SOLUBILITY EFFECTS

The simplest type of SLM used for the extraction of phenol consists of an organic solvent containing no carrier[80-83]. In these systems a pH gradient is maintained across the membrane with the phenol in the feed solution being at low pH and the stripping side being at a high pH. Unionised phenol dissolves in the organic solvent and after diffusing through the membrane then enters the stripping solution where it yields the phenate ion which is virtually insoluble in the SLM. Thus transport against a concentration gradient is possible in this system.

Initially specific long chain alcohols, such as decanol[80], were used as solvents. In batch runs with SLMs formed from 40% decanol in dodecane *ca* 90% extraction was possible within 3 hours. In dynamic runs with the same SLM a flux of 3.5×10^{-5} kg/m^{2}s was achieved for a phenol feed phase concentration of 5g/l. This SLM was stable for 6 days. SLMs containing solvent mixtures have generated great interest as they are very generally stable. The most stable SLMs so far reported are based on a non-polar solvent containing a low concentration of a highly polar solvent. Studies by Salazar[82,83] *et al* have shown that a solvent mixture of kerosene at 82.5% and MIBK at 17.5% are stable for over 2000 hours using a hollow fibre support.

1.6.2 PHENOL EXTRACTION USING AN AMINE CARRIER IN A SLM

Amine based solvent extractants[84-86] are well known and utilise the basic nature of the amine and the acidic nature of the phenol to form a weak complex which has high organic solubility. Long chain tertiary amine extractants are very selective and high yield extractions are possible. Consequently the use of long chain tertiary amines[87-89] as carriers in SLMs is an obvious extension.

Tri-n-octylamine (TOA) has been selected as the carrier in most amine carrier SLM systems[87]. The TOA is dissolved in a solvent, typically an alcohol such as octanol. The feed solution of phenol has a pH of *ca* 5 as at this pH phenol forms an ion-pair complex with the TOA.

$$PhOH + TOA \rightarrow [PhO]^- + [TOAH]^+$$

As the complex reaches the interface at the stripping side, which is at a high pH, decomplexation take place and phenate ion enters the stripping phase and TOA is regenerated.

$$[PhO]^- + [TOAH]^+ + NaOH \rightarrow Na^+[PhO]^- + TOA + H_2O$$

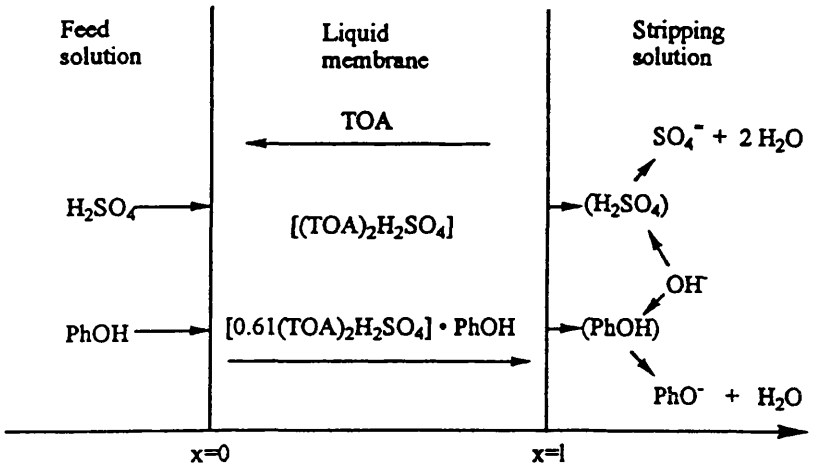
Several groups have shown that using an amine salt rather than the free amine results in more efficient transport of phenol[88.89]. The flux using a TOA salt as a carrier with a 5g/l feed phenol concentration is *ca* 2×10^{-5} mol/m^{2}s, which is about 20% higher than in the amine carrier system above. The higher flux is thought to be due to an increase in the distribution coefficient of the phenol within the organic phase. From equation 1.1 it can be seen that increasing the solubility will increase the flux.

More recently Liu[88] *et al* have used SLMs in which the membranes contain TOA together with a small quantity of sulphuric acid. The acid produces an amine salt with unreacted TOA acting as the diluent .The phenol fluxes were not recorded but the

phenol permeability has been reported to be 8 x 10^{-6} m/s in SLMs with TOA acting as the diluent compared with 6 x 10^{-6} m/s for SLMs with a solvent acting as the diluent. These permeabilities refer to a feed phenol concentration range of 0.1 to 1M. Fluxes increase with increasing permeability so from these results it can be seen that higher fluxes will be achieved by using TOA rather than a solvent as the diluent.

The products of the reaction of TOA and sulphuric acid are many and make interpretation of the role of each species very difficult. They are reported to include $[TOAH]_2SO_4$, $[TOAH]HSO_4$, $[(TOAH)HSO_4]_2$, $[(TOAH)_2SO_4]_2$ and $[(TOAH)_3H(SO_4)_2]$. Work by Wang and Hu[90] has shown that the dimer of the trioctylamine bisulfate salt $[(TOAH)_2SO_4]_2$ is the main product at the low concentration of sulphuric acid usually used. The other products present are at too low a concentration for them to be considered significant in the transport mechanism.

The transport of phenol through such a liquid membrane is illustrated schematically in figure 1.14. The phenol and sulphuric acid in the feed solution diffuse toward the membrane. At the interface the weak complex $[(TOAH)_2SO_4]_2.PhOH$ is formed by the interaction of phenol and trioctylamine bisulphate. This complex then diffuses through the membrane towards the stripping phase interface. The high pH of the stripping phase causes de-complexation with phenate ion and sulphuric acid entering the stripping phase. TOA is regenerated in this reaction and diffuses back to the feed interface, where the trioctylamine bisulphate salt is regenerated. As can be seen from the above mechanism sulphuric acid as well as phenol is transported, so the feed needs to contain a small amount of sulphuric acid.



Extraction : x=0, $2\,(TOA) + H_2SO_4 \rightleftharpoons (TOA)_2H_2SO_4$

$PhOH + 0.61\,(TOA)_2H_2SO_4 \rightleftharpoons [0.61(TOA)_2H_2SO_4] \cdot PhOH$

Stripping : x=l, $(TOA)_2H_2SO_4 + 2\,OH^- \rightleftharpoons 2\,(TOA) + 2\,H_2O + SO_4^{=}$

$[0.61(TOA)_2H_2SO_4] \cdot PhOH + OH^- \rightleftharpoons PhO^- + 0.61\,(TOA)_2H_2SO_4 + H_2O$

Figure 1.14 Transport of phenol in a TOA sulphuric acid salt SLM.

1.6.3 EXTRACTION OF ORGANIC COMPOUNDS USING SLMs BASED ON CROWN ETHER CARRIERS

SLM separations using ether carriers have not received as much attention as those employing amine carriers. A potentially interesting group of ethers are the crown ethers, one reason being that they can act as models for biological systems[91-92]. A wide variety of crown ethers from dibenzo-18-crown-6[93] to complex bis crowns[94] which can form sandwich complexes, have been used in SLM separations. Crown ethers can be highly selective compared with other carriers.

No studies have been carried out using crown ethers to separate phenol, but their use for the separation of other polar compounds such as amino acids[94] and urea[95] has been investigated. It is clear from these studies that crown ethers have potential as carriers for the SLM based separation of phenol. This has been confirmed by crystal structures studies of several adducts of 18-crown-6 with substituted phenols of stoichiometry $(R_nPhOH)_n$.18-crown-6. H_2O, where R= NO_2, n= 1 or 2, showing

hydrogen bonding interactions between phenol and encapsulated water molecules[96,97] (see figure 1.15).

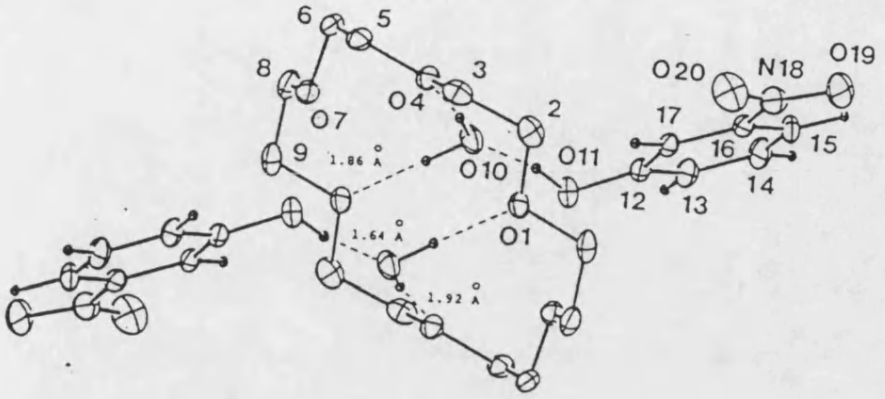


Figure 1.15 A 2:1 complex of 3-nitrophenol and 18-crown-6.

The SLM studies[94,95] involve the use of a high pH feed solution (0.1M NaOH) with a low pH stripping solution. Thus Na^+ ions are transported across the SLM as well as the organic substrate. The Na^+ ions act as co-operative carriers in the transportation of the substrate. The Na^+ ion occupies the central cavity of the crown, and the organic substrate interacts with the bound Na^+ ion. At the membrane/stripping phase interface the low pH causes de-complexation of the Na^+ ions and the substrate which both enter the stripping phase.

1.6.3.1 LIQUID POLGLYCOL SLM

One way to overcome the instability of conventional SLMs is to use a liquid polymer with a carrier chemically attached to the polymer backbone, or a functionality in the polymer backbone, which can act as a carrier. The liquid polymer replaces the organic solvent present in conventional SLMs.

The advantages of using a liquid polymer in this way include;

i) Liquid polymers can often be chosen with very low water solubilities and very low vapour pressures, so increasing the stability of the SLM.

ii) The carriers are chemically bonded to or form part of the polymer chain, so they cannot be lost by partitioning between the organic and aqueous phases.

iii) The chemical functionality on the liquid polymer chain can in some instances be changed in order that a different target substrate may be transported through the membrane.

iv) The physical properties of the liquid polymer can be changed by control of chain length, blending, and crosslinking. This provides an additional measure of control of stability and selectivity.

The only major study of polymeric liquid SLMs so far carried out is by the Monsanto[98] company in 1996. Monsanto produces a large amount of aqueous waste containing *ca* 3% of p-nitrophenol and 15% inorganic salts. This waste is very difficult to treat by traditional methods due to the high salt content. Poly(propylene glycol) (PPG figure 1.16) with a molecular weight of *ca* 4000 Daltons was used for SLM formation. Lower molecular weight polyglycols are water soluble and significantly higher molecular weight polyglycols would give low p-nitrophenol fluxes. The ether linkages can hydrogen-bond to polar organic compounds, including nitrophenol, so facilitating its transport through the membrane.

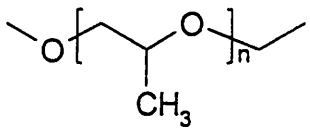


Figure 1.16 Poly(propylene glycol)

Due to its hydrophobic nature PPG forms an effective barrier to the transportation of charged species. It has been shown to exclude both small ions from the dissociation of inorganic salts and large charged organic molecules. Only neutral compounds have reasonable fluxes through PPG. These characteristics form the basis of Monsanto's use of PPG for the separation of nitrophenol in high saline solutions.

The driving force is created by a pH gradient across the SLM. The feed side is kept acidic so that the nitrophenol is unionised and thus is the only component of the feed solution which can enter the membrane. The stripping side a has a high pH so the transported nitrophenol is deprotonated, and as it is then a charged ion it is unable to pass back through the membrane.

The IR spectra of p-nitrophenol, PPG 4000, and a 20% solution of nitrophenol in PPG are shown below in figure 1.17. Hydrogen-bonding between p-nitrophenol and PPG causes the OH stretch of p-nitrophenol to appear as a broad band (centred at *ca* 3190 cm^{-1}) shifted from its position of 3330 cm^{-1} in free p-nitrophenol.

Although the mechanism for the transport of nitrophenol has not been investigated by Monsanto[98], it seems likely that nitrophenol exhibits a "jumping" mechanism from one ether linkage to another, so helping diffusion and increasing the flux.

Liquid polyglycol SLMs have some severe limitations. Firstly the polymer chain is difficult to change chemically so the separations that are possible are very limited by the chemistry of polyglycol. Secondly, as charged species cannot be transported readily many important classes of organic and inorganic substrates cannot be separated using this technique.

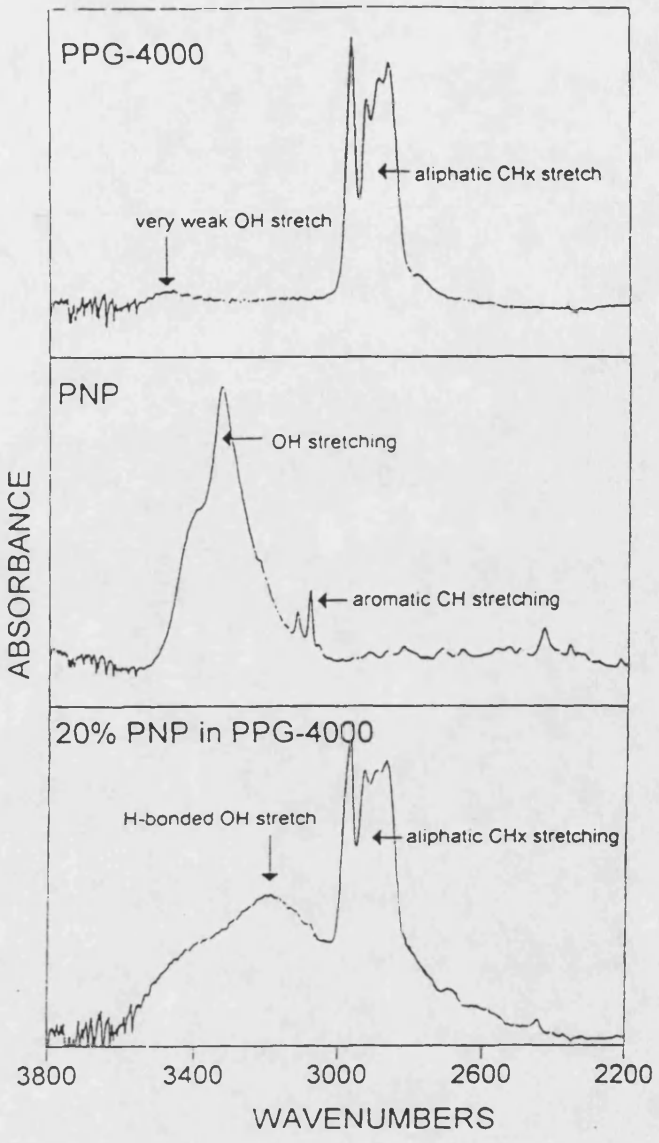


Figure 1.17 FTIR spectra of p-nitrophenol(PNP), PPG-4000 and mixtures of both.

1.7 POLY(ORGANOSILOXANE)S AS AN INTEGRATED SOLVENT/CARRIER SYSTEM.

In this project poly(organosiloxane) fluids have been used as an integrated solvent/carrier system for the separation of phenolic compounds from aqueous solution. Poly(organosiloxane) fluids have many advantages in this respect compared with other liquid polymers. These include:

i) Poly(dimethylsiloxane), from which the poly(organosiloxane)s used within this project are derived, are highly hydrophobic so inhibiting loss of the membrane fluid to the aqueous medium and preventing water incursion into the SLM (see section 1.9).

ii) Organo receptors of various types can easily be added to linear dimethylsiloxane chains using commercial available poly(methylhydridosiloxane)-poly(dimethylsiloxane) co-polymers and an appropriate alkene[99] or alcohol[100]. This makes it possible to design a poly(organosiloxane) for a specific separation as highly selectivity carriers can be added to the siloxane chain.

iii) Poly(dimethylsiloxane) fluids have chemical and physical properties which are highly desirable within a SLM. These include good stability to chemical attack, very low vapour pressure, and high thermal stability. These properties are to some degree passed onto the type of functionalised poly(organosiloxane)s used in this project.

1.8 INDUSTRIAL PRODUCTION OF POLYSILOXANES

Silica is the raw material for the production of elemental silicon. It is usually reduced to the element with high purity coke in an electric arc furnace[101] at approximately 1000^0C.

$$SiO_2 + 2C \rightarrow Si + 2CO$$

The silicon can then be converted directly to tetrachlorosilane[102] by the reaction of chlorine gas at *ca* 350^0C.

$$Si + 2Cl_2 \xrightarrow{\Delta} SiCl_4$$

The tetrachlorosilane may than be converted to a diorganodichlorosilane using a Grignard reagent[102]. The diorganodichlorosilane is then hydrolysed to form siloxanes. Grignard synthesis is no longer commercially employed for the production of

dimethylchlorosilane (intermediate for PDMS) but it is still used for the production of specialised siloxanes.

$$SiCl_4 \xrightarrow{RMgX} MgClX + RSiCl_3 + R_2SiCl_2 + R_3SiCl + R_4Si$$

The mono- and dichloro-silanes serve as starting materials for the preparation of mixed alkyl or arylchlorosilanes.

$$RSiCl_3 \xrightarrow{R'MgX} MgClX + RSiR'Cl_2 + R'_2SiRCl + R'_3SiR$$

This relatively expensive alkylation procedure has been largely replaced by the Direct process, sometimes called the Rochow process[103,104], which starts from elemental silicon. Rochow found that alkyl and aryl halides react directly with silicon when their vapours come into contact with the solid at temperatures greater than 300^0C in the presence of a catalyst. The reaction is promoted by a wide variety of metals but the most efficient catalyst is copper, and under these conditions a complex mixture of organosilicon halides are produced.

$$MeCl + Si \xrightarrow[Cu]{>300\ ^\circ C} \begin{cases} Me_2SiCl_2 \text{ (bp 70 °C; 30–80 \%)} \\ MeSiCl_3 \text{ (bp 66 °C; 10–40\%)} \\ Me_3SiCl \text{ (bp 57.7 °C)} \\ SiCl_4 \text{ (bp 57.6 °C)} \\ MeSiHCl_2 \text{ (bp 40.7 °C)} \\ SiCl_3H \text{ (bp 31.8 °C)} \end{cases}$$

Figure 1.18 Rochow process.

The Rochow process produces all possible substitutions of the chlorosilanes as shown in figure 1.18. Under the right conditions the yield of the desired product, R_2SiCl_2, can be as high as 90%. Other products are removed by fractional distillation. The mechanism[105] of the reaction has not yet been fully evaluated but evidence points to

the formation of a Si-Cu compound that more readily polarises the C-Cl bonds than either Si or Cu alone to generate methyl radicals and reactive silicon chlorides.

$$MeCl + (Si\text{-}Cu) \rightarrow [MeCuCl] \rightarrow Me^{\cdot} + CuCl + Si$$

$$CuCl + Si \rightarrow [SiCl] + Cu$$

$$[SiCl] + Me^{\cdot} \rightarrow MeSiCl \rightarrow Me_xSiCl_{4-x} \quad (x = 1\text{-}3)$$

Figure 1.19 Mechanistic features of the Rochow process.

$$R_2SiCl_2 + 2H_2O \rightarrow R_2Si(OH)_2 + 2HCl$$

$$X[R_2Si(OH)_2] \rightarrow [R_2SiO]_x + XH_2O$$

The siloxanes are produced by the hydrolysis of R_2SiCl_2 which forms silanols as intermediates which than condense to form the various siloxanes. The nature of the siloxane produced depends critically on the reaction conditions. Basic catalysts and high temperatures favour high molecular weight linear products. Acidic catalysts tend to produce cyclic, and low molecular weight linear siloxanes.

1.8.1 RING-OPENING POLYMERISATION

The direct production of high molecular weight polysiloxanes by the hydrolysis of R_2SiCl_2 has now been largely replaced by ring-opening polymerisation[106-108] of cyclic trimer and tetramer siloxanes. Ring-opening polymerisation is usually initiated by anionic initiators. In principle the reaction is reversible, but in practice it is made essentially irreversible by the choice of monomer, initiator, and polymerisation conditions. Typical anionic catalysts are alkali metal oxides, hydroxides and siloxides. Initiation and propagation involve nucleophilic attack on the cyclic monomer, causing opening of the ring followed by chain extension.

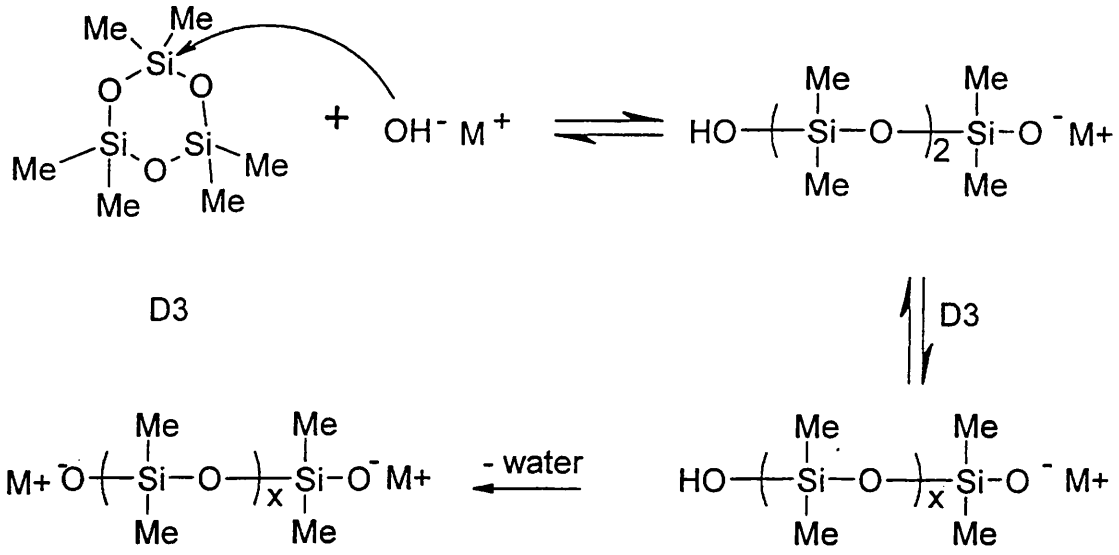


Figure 1.20 Mechanism of ring opening polymerisation.

Polymerisation of the tetramer is very different from most polymerisations which are enthalpy driven. In this ring-opening reaction, the bonds formed are of similar energy to those in the ring. The driving force for the reaction is the change in entropy, as the linear polymer has a much higher molecular freedom than that of the ring compound.

Co-polymers can be produced by two methods. The first involves the use of cyclic siloxanes which have different R groups $[(SiR_2O)(SiR'_2O)]_n$, and the second method is based on the ring opening of a cyclic siloxane in the presence of $R'_2Si(OH)_2$. The poly(dimethylsiloxane)-(methylhydridosiloxane) co-polymers used in this project are formed from ring opening hydrolysis of $(Me_2SiO)_4$ in the presence of $MeSi(H)(OH)_2$. The resulting co-polymers are random co-polymers.

1.9 STRUCTURE AND PROPERTIES OF POLY(ORGANOSILOXANE)S

Poly(dimethylsiloxane) (PDMS) is the most common commercially available poly(organosiloxane). PDMS has unusual chemical and physical properties, completely different to those of most organic polymers, which gives rise to unique and a very large number of applications of PDMS. One of the most unusual properties of PDMS is its very low glass transition temperature,[109] (T_g), which at -125 ^{0}C is the lowest of all the commonly available polymers. The glass transition temperature[110] signifies the sharp change from the "glassy" state in which the polymer is rigid and brittle to a "rubbery" state in which the polymer shows a degree of elastomeric-type properties i.e. impact resistance, elasticity, ability to creep and to swell in solvents.

The glass transition temperature is determined by a number of factors, one of the most important of which is the flexibility of the main polymer chains. Chain flexibility depends on the ability of the skeletal bonds to rotate without causing significant changes in O-Si-O bond angle or bond length. Also important in determining T_g is the mobility and size of the side chains. Large side groups or polar interactions between side groups, will cause the groups to repel or attract each other, so lowering the mobility of the groups and hence increasing T_g. For this reason the introduction of phenyl side groups increases T_g. Thus the T_gs of $(PhMeSiO)_n$ and $(Ph_2SiO)_n$ are -86°C and ~0°C respectively compared to -125°C for PDMS.

The reason for the very low T_g for PDMS can also be understood by examining the bonding in PDMS. The Si-O skeletal bond[110] has a bond length of 1.64 Å whereas the C-C single bond present in most organic homopolymers has a bond length of 1.53 Å. The longer Si-O bond tends to reduce the steric hindrance between substituents. This is partly negated by the larger size of Si compared with C, but not completely. T_g is also determined by the size and mobility of the side groups and as the skeletal oxygen atoms have no side groups, the methyl substituents on Si have a large amount of freedom to

move with a resultant very low rotational barrier. All these features contribute to the great flexibility of segments of PDMS hence lowering its T_g.

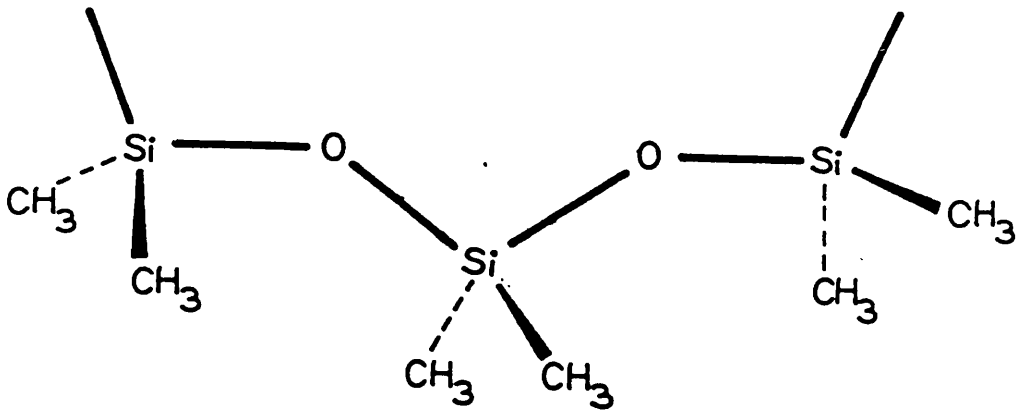


Figure 1.21 Structure of PDMS.

The preferred low energy state of PDMS is reached with the backbone folded into a coil so that an individual siloxane chain has low spatial extension. This results from the large difference between successive Si-O-Si (143°) and O-Si-O (112°) bond angles in the chain in which the O-Si-O bond angle is relative ridged but the Si-O-Si angle is flexible. PDMS exhibits only weak temperature dependence of many of its physical properties including viscosity, as on heating the number of higher energy states available increases, resulting in the siloxane chain unfolding (figure 1.22) and creating a greater distance between the ends of individual siloxane chains. Thus an increasing molecular entanglement compensates for the normal increase in molecular mobility with increasing temperatures.

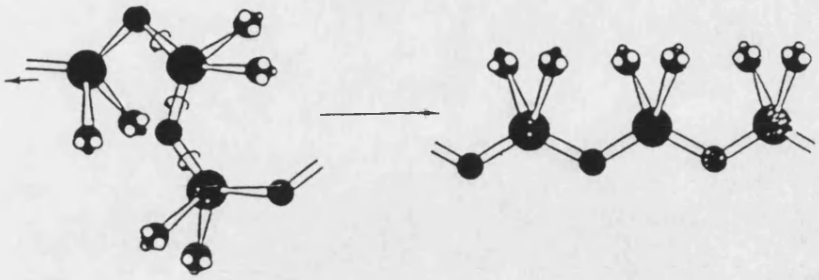


Figure 1.22 Stretching of siloxane chain.

The basic differences between silicon[111] and carbon chemistry can explain some of the other properties of polysiloxanes. Silicon is more electropositive than carbon. Bonds between silicon and Cl, N, O, and S are more ionic and have higher average bond energies than those to carbon. Bonds between Si-C and Si-H bonds have lower bond energies than C-C and C-H bonds (table 1.2).

The nature of the Si-O bond is influenced by electronegativity differences, with the Si-O bond being *ca* 50% ionic with silicon being electropositive. The Si-O bond is resistant to homolytic cleavage but it is susceptible to heterolytic cleavage by both acids and bases. This reaction is utilised in ring-opening polymerisation reaction (see section 1.8.1). The Si-CH_3 bond is not susceptible to heterolytic cleavage as it is only slightly polar, and the Si-C bond energy is very comparable to the C-C bond energy.

The Si-H bond is reactive and far more susceptible to heterolytic cleavage than the C-H bond. Silane (SiH_4) it is spontaneously flammable in air and it is readily hydrolysed by water whereas methane by comparison is very inert. There are several factors which contribute to this difference. Firstly the larger Si radius compared to C facilitates attack by nucleophiles. Secondly the greater polarity of the Si-H bond contributes to its reactivity, as does the presence of low lying d orbitals on Si. The reactivity of Si-H bonds provides an important synthetic pathway to form organosiloxanes which will be discussed in section 1.10.

reactivity of Si-H bonds provides an important synthetic pathway to form organosiloxanes which will be discussed in section 1.10.

X	C	Si	H	Cl	O
C-X	370	360	435	350	360
Si-X	360	340	395	380	450

Table 1.2 Average bond energies in kJ mol^{-1}.

1.10 SYNTHESIS OF POLY(ORGANOSILOXANE)S

A major synthetic pathway leading to specialised organofunctional siloxanes involves synthetic manipulations of commercially available poly(dimethylsiloxane)-(methylhydridosiloxane) co-polymers. This synthetic route has been used for many years at Bath University[86,94,121] and it has been used in this project. These co-polymers undergo two main types of reaction which are important in the context of this research project;

i) Hydrosilylation.
ii) Reaction of Si-H groups with hydroxyl groups.

1.10.1 HYDROSILYLATION

Hydrosilylation is very commonly used to prepare organofunctional siloxanes and has been the preferred method of producing specialised organofunctional siloxanes containing direct Si-C linkages in this department. In hydrosilylation[112-116] of poly(dimethylsiloxane)-(methylhydridosiloxane) co-polymers Si-H addition across an α-alkene yields a new Si-C bond. In the absence of any catalyst the reaction needs temperatures in the region of 300°C and elevated pressures. The reaction is readily catalysed either by radical initiators, or more commonly by certain transition metal complexes.

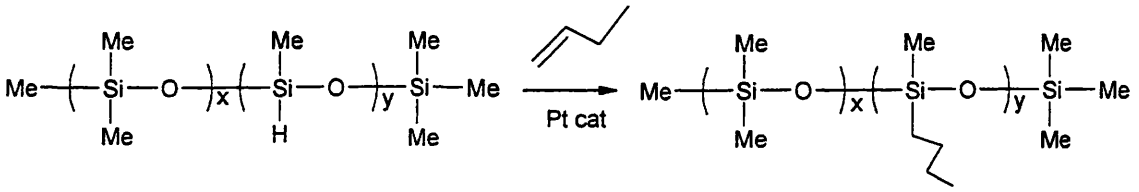


Figure 1.23 Hydrosilylation of a 1-alkene by a poly(dimethylsiloxane)-(methylhydridosiloxane) co-polymer.

The most common catalyst used in this reaction is chloroplatinic acid, $H_2PtCl_6.6H_2O$, known as Speier's catalyst. This is often active at room temperature but it is more frequently used at *ca* 80-100^{0}C in solvents such as tetrahydrofuran or toluene[110-112] which dissolves poly(organosiloxane)s and does not interfere with the hydrosilylation. The mechanism is still not well understood. In the first proposed mechanism suggested by Chalk and Harrod[117] the catalytic system was thought to be homogeneous but work by Lewis and Lewis[118] has shown that it is often heterogeneous with the active species in the colloidal state. The mechanism is believed to involves oxidative addition of Si-H to $Pt^{(0)}$, followed by co-ordination of the alkene to platinum. Rearrangement and final reductive elimination of the organofunctional siloxane then occurs.

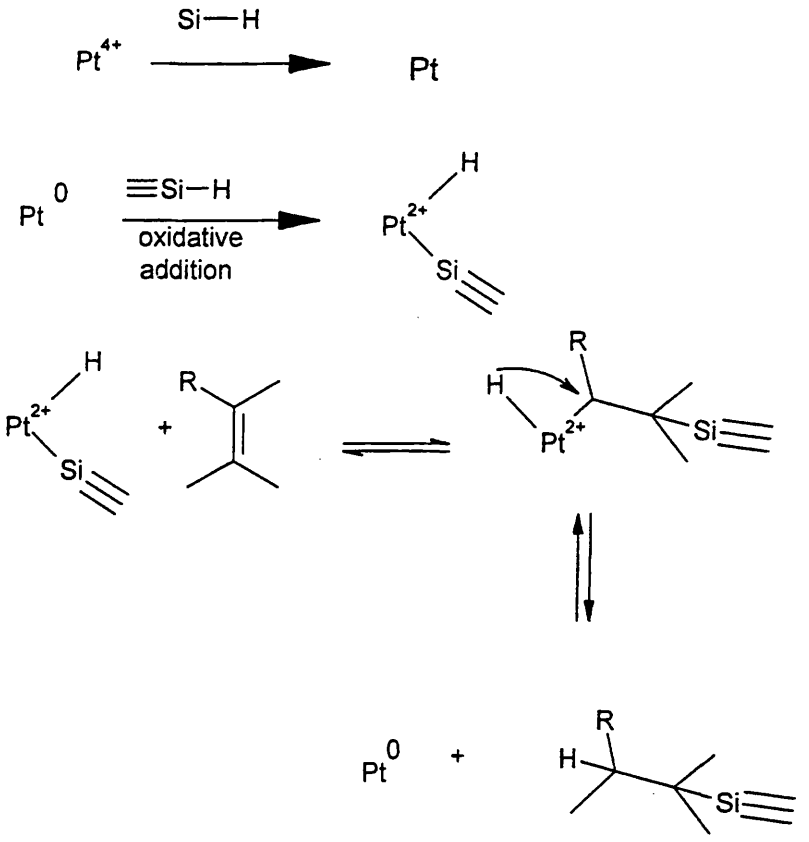


Figure 1.24 Mechanism of hydrosilylation.

Two products are possible the major product, usually with a yield greater than 90%, is the linear derivative[118].

$$2R_2Si(H)OSiR_3 + 2CH_2{=}CHCH_3 \rightarrow \underset{\text{major product}}{R_3SiOR_2Si\text{-}CH_2CH_2CH_3} + \underset{\text{minor product}}{R_3SiOR_2Si\text{-}CH(CH_2)CH_3}$$

1.10.2 REACTION WITH HYDROXYL GROUPS

Hydroxyl containing compounds such as primary alcohols react with poly(dimethylsiloxane)-(methyl hydridosiloxane) co-polymers in the presence of a variety of metal catalysts to form Si-O-C containing species with elimination of hydrogen. The most commonly used catalysts are zinc octanoate, iron octanoate, and dibutyltin dilaurate[119,120], but Pt species are also effective. Although high loadings are

readily achieved the resultant poly(organosiloxane) fluid contains Si-O-C linkages which are weaker than the Si-C-C linkages which are formed in hydrosilylation.

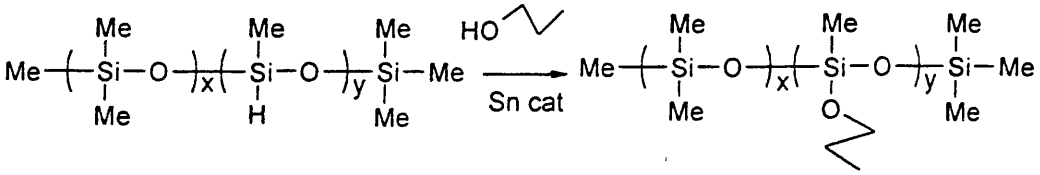


Figure 1.25 Reaction of a primary alcohol with poly(dimethylsiloxane)-(methylhydridosiloxane) co-polymer

The industrial production of siloxane co-polymers[121] utilises the reaction of water with an alkoxysilane catalysed by dibutyltin dilaurate (DBTDL). The reaction involves a hydrolysis step in which the silane methoxy groups form silanol groups (1) and a condensation step in which these silanol functionalities condense (2).

$$\text{-Si-OCH}_3 + \text{H}_2\text{O} \rightarrow \text{-Si-OH} + \text{CH}_3\text{OH} \quad (1)$$

$$\text{-Si-OH} + \text{-Si-OH} \rightarrow \text{-Si-O-Si} + \text{H}_2\text{O} \quad (2)$$

In the mechanism proposed by van der Weij[122] DBTDL itself undergoes a hydrolysis reaction and forms an organotin hydroxide (figure 1.26) and it is that compound which is the actual catalyst. The organotin hydroxide further reacts with an alkoxysilane to form an organotin silanolate (Sn-O-Si). It is further proposed[122] that the organotin silanolate is able to react with silanols to form the Si-O-Si crosslink.

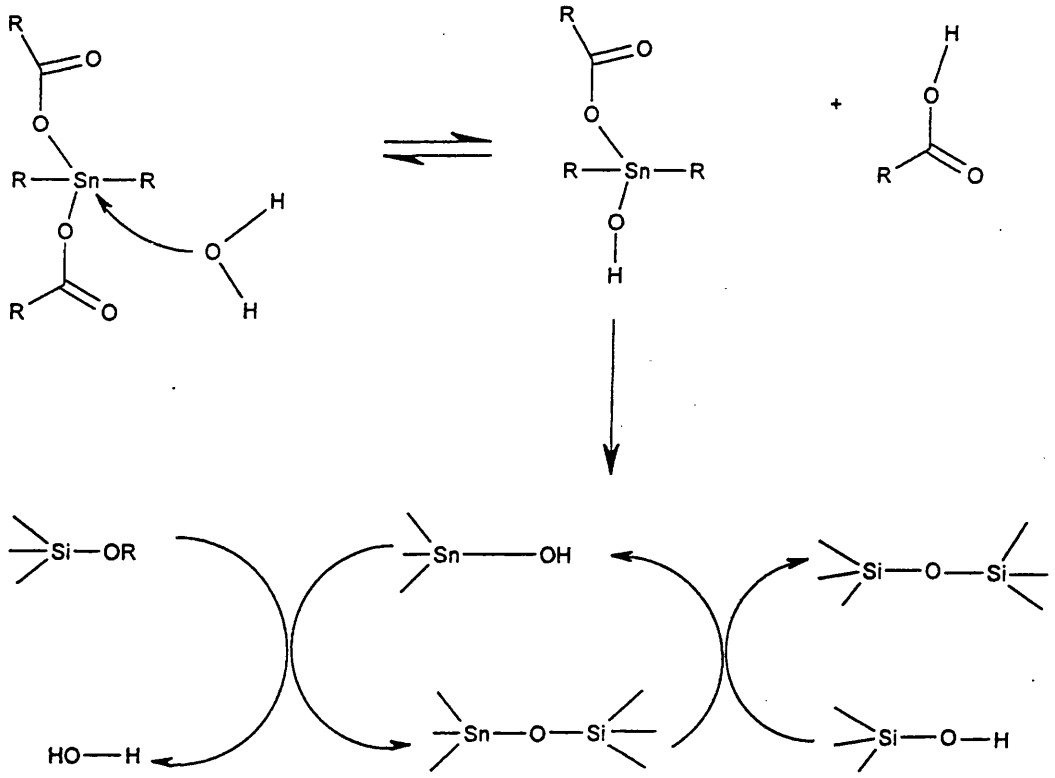


Figure 1.26 Mechanism for the hydrolysis of an alkoxysilane.

CHAPTER 2

MATERIALS AND METHODS

2.0 MATERIALS AND METHODS

This chapter contains a complete description of the experimental and analytical procedures used in this investigation. The synthesis of several poly(organosiloxane) fluids and model organofunctional trisiloxanes are also described. The specifications of the test SLM rig are outlined together with the procedures used in the running of the rig and the analysis of the substrates.

2.1 REAGENTS

The siloxane co-polymers (3-4%)-methylhydrido-(96-97%)-dimethylsiloxane co-polymer, (15-18%)-methylhydrido-(82-85%)-dimethylsiloxane co-polymer, (30-35%) methylhydrido-(65-70%)-dimethylsiloxane co-polymer and the trisiloxane 1,1,1,3,5,5,5-heptamethyltrisiloxane were purchased from Flurochem, stored over 4Å molecular sieves and used without further purification.

The alcohols ethyl 6-hydroxyhexanoate, butanol, 3-N,N-dimethylamine-1-propanol, and ethoxyethanol were all purchased from Aldrich and stored over 4 Å molecular sieves.

Chemicals used in the synthesis of the catalyst dichloro(1,5-cyclooctadiene) platinum(II) were purchased from Aldrich and used directly. The test substrates phenol, benzyl alcohol, bromophenol, methoxyphenol, hydroquinone were all purchased from Aldrich and they were used directly.

2.2 CHARACTERISATION

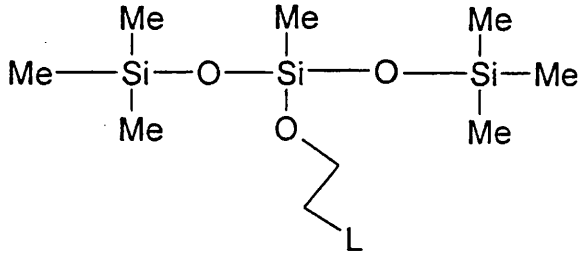
Infrared spectra were recorded on a Nicolet 570P FTIR instrument using NaCl plates. Data are reported as peak maxima (ν_{max}) in wavenumbers (cm^{-1}).

NMR spectra were recorded at room temperature on JEOL 270 or 400 MHz NMR instruments. Chemical shifts are reported in ppm downfield from tetramethysilane (TMS) but were measured for ^{1}H and ^{13}C nuclei relative to residual ^{1}H and ^{13}C resonances in $CDCl_3$. ^{29}Si chemical shifts are reported relative to TMS. Samples contained 0.02M $Cr(acac)_3$ to help relaxation.

Miroanalyses for C, H, and N were performed by Mr A. Carver on a Carlo Erba 1106 Elemental Analyser at the University of Bath.

2.3 PREPARATION OF MODEL ORGANOTRIOSILOXANES

Four model organotrisiloxanes were synthesised, each with a different organic functional group chemically linked to the central Si atom of the trisiloxane. They have the general formula:



L = $CH_2N(Me)_2$	compound M1
L = OEt	compound M2
L = CH_2CH_3	compound M3
L = $(CH_2)_4CO_2$ Et	compound M4

2.3.1 PREPARATION OF THE AMINE FUNCTIONALISED TRISILOXANE M1

1,1,1,3,5,5,5-Heptamethyltrisiloxane (2.00g, 9.0mmoles) was added to a flame dried 25cm^3 single necked flask fitted with a condenser. 3-Dimethylaminepropanol (0.92g, 9.0mmoles) was treated with the catalyst dichloro(1,5-cyclooctadiene) platinum(II) (10mg, 2.67x10^{-5}moles) and added to the trisiloxane. The reaction mixture was heated at 85°C under a nitrogen atmosphere for 24 hours at which point a further quantity of catalyst (10mg, 2.67x10^{-5}moles) in dimethylaminepropanol (0.1g, 0.9mmole) was added. The mixture was then heated for a further 12 hours at 85°C under a nitrogen atmosphere. The reaction mixture was finally distilled under vacuum at 50°C and 0.1mm of Hg to yield the required product as a mobile colourless oil.

Yield 2.65g (98%)

Analysis. (calculated for $C_{12}H_{33}O_3Si_3N$) Found N, 4.34 (4.33); C, 44.2 (44.6); H, 10.4 (10.2) %

^{1}H NMR (ppm, $CDCl_3$) 0.07 (21H, s, Si-CH_3), 1.84 (2H, m, CH_2), 2.10 (6H, s, N-$(CH_3)_2$), 2.23 (2H, t, N-CH_2), 3.64 (2H, t, O-CH_2)

^{13}C NMR (ppm, $CDCl_3$) 1.8 (Si-C), 45.5 (N-CH_3), 31.8, 58.6, 62.3, (CH_2)

^{29}Si NMR (ppm, $CDCl_3$) 8.2 (Me_3SiO), -57.3 ($MeSiO_3$)

IR (cm^{-1}) 2963, 2905, 1653, 1411, 1259, 1020, 866.

2.3.2 PREPARATION OF THE ETHYL ETHER FUNCTIONALISED TRISILOXANE M2

1,1,1,3,5,5,5-Heptamethyltrisiloxane (2.00g, 9.0mmoles) was added to a flame dried 25cm^3 single necked flask fitted with a condenser. 2-Ethoxyethanol (0.82g, 9.0mmoles) was treated with the catalyst dichloro(1,5-cyclooctadiene)platinum(II) (10mg, 2.67x10^{-5}moles) and added to the trisiloxane. The reaction mixture was heated at 85°C under a nitrogen atmosphere for 24 hours at which point a further quantity of catalyst (10mg, 2.67x10^{-5}moles) in ethoxyethanol (0.1g, 1.1mmoles) was added. The mixture was then heated for a further 18 hours at 85°C under a nitrogen atmosphere. The reaction mixture was finally distilled under vacuum at 80°C and 1.0mm of Hg to yield the required product as a mobile colourless oil.

Yield 2.65g (95%)

Analysis. (calculated for $C_{11}H_{30}O_4Si_3$) Found C, 41.8 (42.6); H 9.51 (9.75) %

^{1}H NMR (ppm, $CDCl_3$) 0.10 (21H, s, Si-CH_3), 1.20 (3H, t, CH_3), 3.5 (4H, m, CH_2-O), 3.79 (2H, t, CH_2-O)

^{13}C NMR (ppm, $CDCl_3$) 1.6 (C-Si), 15.2 (CH_3), 61.4, 66.6, 71.5 (CH_2-O)

^{29}Si NMR (ppm, $CDCl_3$) 8.2 (Me_3SiO), -57.4 ($MeSiO_3$)

IR (cm^{-1}) 2959, 2872, 1251, 1064, 970, 843.

2.3.3 PREPARATION OF A n-BUTYL FUNCTIONALISED TRISILOXANE M3

1,1,1,3,5,5,5-Heptamethyltrisiloxane (2.00g, 9.0mmoles) was added to a flame dried 25cm^3 single necked flask fitted with a condenser. 1-Butanol (0.67g, 9.0mmoles) was treated with dichloro(1,5-cyclooctadiene)platinum(II) (10mg, 2.67x10^{-5} moles) and added to the trisiloxane. The reaction mixture was heated at 85°C under a nitrogen atmosphere for 24 hours at which point a further amount of catalyst (10mg, 2.67x10^{-5} moles) in butanol (0.1g, 1.4mmoles) was added. The mixture was then heated for a further 24 hours at 85°C under a nitrogen atmosphere. The reaction mixture was distilled finally under vacuum at 100°C and 1.0mm of Hg to yield the required product as a mobile colourless oil.

Yield 2.50g (94%)

Analysis. (calculated for $C_{11}H_{30}O_3Si_3$) Found C, 44.6 (44.9); H, 10.1 (10.2) %

^1H NMR (ppm, $CDCl_3$) 0.10 (21H, s, Si-CH_3), 0.91 (3H, t, CH_3),1.33 (2H, m, CH_2), 1.51 (2H, m, CH_2), 3.65 (2H, t, O-CH_2)

^{13}C NMR (ppm, $CDCl_3$) 1.6 (C-Si), 13.9, 19.0 (CH_2), 34.6 (CH_3) 61.9 (O-CH_2)

^{29}Si NMR (ppm, $CDCl_3$) 8.2 (Me_3SiO), -57.4 ($MeSiO_3$)

IR (cm^{-1}) 2959, 2874, 1251, 1060, 843, 754.

2.3.4 PREPARATION OF AN ETHYL ESTER FUNCTIONALISED TRISILOXANE M4

1,1,1,3,5,5,5-Heptamethyltrisiloxane (2.00g, 9.0mmoles) was added to a flame dried $25cm^3$ single necked flask fitted with a condenser. Ethyl-6-hydroxy-hexanoate (1.45g, 9.0mmoles) was treated with the catalyst dichloro(1,5-cyclooctadiene) platinum(II) (10mg, $2.67x10^{-5}$ moles) and added to the trisiloxane. The reaction mixture was heated at 85°C under a nitrogen atmosphere for 24 hours at which point a further quantity of catalyst (10mg, $2.67x10^{-5}$moles) in ethyl-6-hydroxy-hexanoate (0.1g, 0.6mmole) was added. The mixture was then heated for a further 24 hours at 85°C under a nitrogen atmosphere. The reaction mixture was finally distilled under vacuum at 120°C and 1.0mm of Hg to yield the required product as a mobile colourless oil.

Yield 3.25g (95%)

Analysis. (calculated for $C_{15}H_{36}O_5Si_3$) Found C, 48.0 (47.4); H, 9.50 (9.47) %

^1H NMR (ppm, $CDCl_3$) 0.08 (21H, s, Si-CH_3), 1.22 (3H, t, CH_3), 1.34 (2H, q, CH_2), 1.58 (2H, q, CH_2), 1.61(2H, q CH_2), 2.27(2H, t, CH_2-CO), 3.61(2H, t, O-CH_2), 4.01(2H, q, O-CH_2)

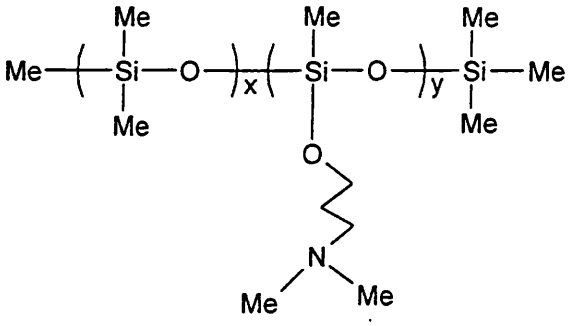
^{13}C NMR (ppm, $CDCl_3$) 1.6 (C-Si), 14.2, 24.6, 25.4, 32.1, 34.3,(CH_2), 60.1, 61.8,(CH_2-O), 173.7 (C-O_2)

^{29}Si NMR (ppm, $CDCl_3$) 8.3 (Me_3SiO), -57.4 ($MeSiO_3$)

IR (cm^{-1}) 2959, 2870, 1740, 1458, 1373, 1251, 1161, 1059, 844.

2.4 PREPARATION OF AMINE FUNCTIONALISED LINEAR POLY(ORGANOSILOXANE) FLUIDS

Three amine functionalised poly(organosiloxane)s were synthesised, each with a different mole ratio of amine attached to the siloxane backbone. Their general formula was:



A1 4 mole % amine, X = 179, Y = 9

A2 11 mole % amine, X = 24, Y = 3 or 4 (average 3.5)

A3 30 mole % amine, X =18, Y = 9

2.4.1 PREPARATION OF A 4 MOLE % AMINE FUNCTIONALISED POLY(ORGANOSILOXANE) A1

(4%)-Hydridomethylsiloxane-(96%)-dimethylsiloxane co-polymer (10.0g, 0.75mmoles) was added to a flame dried 50cm^3 single necked flask fitted with a condenser. 3-Dimethylaminepropanol (0.68g, 6.75mmoles) was treated with the catalyst dichloro(1,5- cyclooctadiene)platinum(II) (10mg, 2.67x10^{-5} moles) and then added to the flask. The reaction mixture was heated at 80°C under a nitrogen atmosphere for 24 hours then a further amount of catalyst (10mg, 2.67x10^{-5} moles) in dimethylaminepropanol (0.1g, 0.9mmoles) was added and heating of the mixture continued for a further 72 hours at 80°C. The reaction mixture was then treated with 20cm^3 of dichloromethane, the resulting solution filtered, and the dichloromethane removed using a rotary evaporator. The residual oil was finally held at 80°C at 0.1 mm Hg pressure for 2 hours to remove volatiles.

Hydride replaced by amine functionality 86% (by ^{1}H NMR)

Analysis (calculated assuming 100% Si-H replacement, $C_{400}H_{1173}O_{189}N_9Si_{181}$)

Found N, 0.67 (0.88); C, 33.30 (33.82); H, 8.26 (8.26) %

^{1}H NMR. (ppm, $CDCl_3$) 0.05 (s, Si-CH_3), 1.85 (m, CH_2), 2.10 (s, N-$(CH_3)_2$), 2.28 (t, N-CH_2), 3.63 (t, O-CH_2)

IR(cm^{-1}) 2963, 2905, 1601, 1446, 1261,1020, 800.

2.4.2 PREPARATION OF A 11 MOLE % AMINE FUNCTIONALISED POLY(ORGANOSILOXANE) A2

This reaction was carried out as above using a (12%)-hydridomethylsiloxane-(88%)-dimethylsiloxane co-polymer (10.0g, 4.0mmoles) and 3-dimethylaminepropanol (1.54g, 15.0mmoles).

Hydride replaced by amine functionality 92% (by ^{1}H NMR)

Analysis (calculated assuming 100% Si-H replacement, $C_{77}H_{215}N_4O_{32}Si_{30}$)

Found N, 2.00 (1.96); C, 35.9 (36.0); H, 8.53 (8.57) %

^{1}H NMR. (ppm, $CDCl_3$) 0.05 (s, Si-CH_3), 1.85 (m, CH_2), 2.21 (s, N-$(CH_3)_2$), 2.28 (t, N-CH_2), 3.71 (t, O-CH_2)

IR (cm^{-1}) 2963, 2876, 2766, 1462, 1412, 1261,1018, 798.

2.4.3 PREPARATION OF A 30 MOLE % AMINE FUNCTIONALISED POLY(ORGANOSILOXANE) A3

This reaction was carried out as above using a (31%)-methyhydridolsiloxane-(69%)-dimethylsiloxane co-polymer (10.0g,4.8mmoles) and 3-dimethylaminepropanol (4.89g, 48mmoles).

Hydride replaced by amine functionality 97% (by ^{1}H NMR)

Analysis (calculated assuming 100% Si-H replacement, $C_{96}H_{261}N_9O_{37}Si_{29}$)

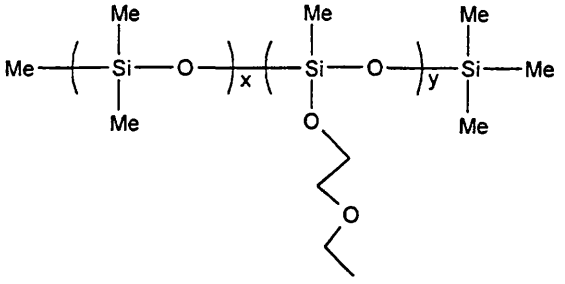
Found N, 4.40 (4.47); C, 40.8 (40.9); H, 9.20 (9.22) %.

^{1}H NMR. (ppm, $CDCl_3$) 0.06 (s, Si-CH_3), 1.85 (m, CH_2), 2.19 (s, N-$(CH_3)_2$), 2.31 (t, N-CH_2), 3.70 (t, O-CH_2)

IR (cm^{-1}) 2963, 2905, 2816, 2766, 1412, 1261, 1018, 798.

2.5 PREPARATION OF ETHYL ETHER FUNCTIONALISED LINEAR POLY(ORGANOSILOXANE) FLUIDS

Three ether functionalised poly(organosiloxane)s were synthesised each with a different mole ratio of ether. They have the general formula:



E1 4 mole % ether, X = 179, Y = 9

E2 11 mole % ether, X = 24, Y = 3 or 4 (average 3.1)

E3 29 mole % ether, X = 18, Y = 8 or 9 (average 8.5)

2.5.1 PREPARTION OF A 4 MOLE % ETHYL ETHER FUNCTIONALISED POLY(ORGANOSILOXANE) E1

(4%)-Methylhydrosiloxane-(96%)-dimethylsiloxane co-polymer (10.0g, 0.75mmoles) was added to a flame dried 50cm^3 single necked flask fitted with a condenser. 2-Ethoxyethanol (0.67g, 7.5mmoles) was first treated with the catalyst dichloro(1,5-cyclooctadiene)platinum(II) (10mg, 2.67x10^{-5} moles) and then added to the flask. The reaction was stirred and heated at 80°C under a nitrogen atmosphere for 24 hours, then a further quantity of catalyst (10mg 2.67x10^{-5} moles) in ethoxyethanol (0.1g, 1.1mmoles) was added and heating continued at 80°C for a further 72 hours. The reaction mixture was dissolved in 20cm^3 of dichloromethane, then filtered to remove traces of platinum and the dichloromethane then removed using a rotary evaporator. The reaction mixture was finally heated to 70°C at 0.1 mm Hg pressure for 2 hours to remove volatiles.

Hydride replaced by ether functionality 86% (by ^{1}H NMR)

Analysis. (calculated assuming 100% Si-H replacement, $C_{401}H_{1176}O_{203}Si_{186}$)

Found C, 33.3 (33.3); H, 8.37 (8.14) %

^{1}H NMR (ppm, $CDCl_3$) 0.06 (s, Si-CH_3), 1.18 (t, CH_3), 3.50 (m, CH_2), 2.82 (t, CH_2)

IR (cm^{-1}) 2963, 2905, 2816, 2766, 1444, 1260,1022, 798.

2.5.2 PREPARATION OF A 11 MOLE % ETHYL ETHER FUNCTIONALISED POLY(ORGANOSILOXANE) E2

This reaction was carried out as above using a (12%)-methylhydridosiloxane-(88%)-dimethylsiloxane co-polymer (10.0g, 4.0mmoles) and 2-ethoxyethanol(1.44g, 16mmoles)

Hydride replaced by ether functionality 92% (by ^{1}H NMR)

Analysis (calculated assuming 100% replacement, $C_{65}H_{204}O_{36}Si_{29}$)

Found C, 33.00 (32.97); H, 8.65 (8.62) %

^{1}H NMR. ($CDCl_3$) 0.08 (s, Si-CH_3), 1.18 (t, CH_3), 3.52 (m, CH_2), 3.83 (t, CH_2)

IR (cm^{-1}) 2984, 2872, 2816, 1444, 1261, 1022, 800.

2.5.3 PREPARATION OF A 29 MOLE % ETHYL ETHER FUNCTIONALISED POLY(ORGANOSILOXANE) E3

This reaction was carried out as above but using a (31%)-methylhydrosiloxane-(69%)-dimethylsiloxane co-polymer (10.0g, 4.8mmoles) and 2-Ethoxyethanol (4.32g, 48mmoles).

Hydride replaced by ether functionality 94% (by ^{1}H NMR)

Analysis (calculated assuming 100% Si-H replacement, $C_{84}H_{234}O_{46}Si_{29}$)

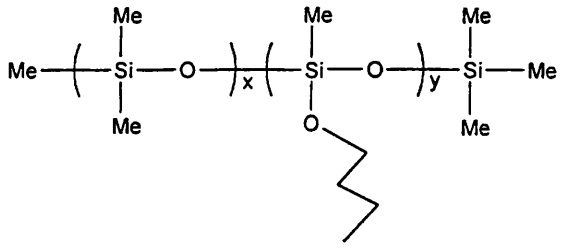
Found C, 35.7 (36.1) ; H, 8.24 (8.26) %

^{1}H NMR (ppm, $CDCl_3$) 0.06 (s, Si-CH_3), 1.18 (t, CH_3), 3.50 (m, CH_2), 3.82 (t, CH_2)

IR (cm^{-1}) 2984, 2872, 2816, 1444, 1261, 1022, 800.

2.6 PREPARATION OF n-BUTYL SUBSTITUTED LINEAR POLY(ORGANOSILOXANE) FLUIDS

Three alkyl substituted poly(organosiloxane)s were synthesised each with a different degree of loading of the alkyl substitution. They have the general formula:



B1 4 mole % alkyl, X = 179, Y = 9

B2 11 mole % alkyl, X = 24, Y = 3 or 4 (average 3.1)

B3 30 mole % alkyl, X = 18, Y = 9

2.6.1 PREPARATION OF A 4 MOLE % n-BUTYL FUNCTIONALISED POLY(ORGANOSILOXANE) B1

(4%)-Methylhydridosiloxane-(96%)-dimethylsiloxane co-polymer (10.0g, 0.75mmol) was added to a flame dried 50cm^3 single necked flask fitted with a condenser. Butanol (0.56g, 7.5mmol) was treated with the catalyst dichloro(1,5-cyclooctadiene)platinum(II) (10mg, 2.67x10^{-5} moles) and then added to the siloxane. The reaction mixtures was stirred and heated at 80°C under a nitrogen atmosphere for 24 hours then a further 10mg of catalysis in n-butanol (0.1g, 1.0 mmol) was added. Heating was continued for a further 72 hours at 80°C. The reaction mixture was then treated with 20cm^3 of dichloromethane, filtered and the dichloromethane removed using a rotary evaporator. The reaction mixture was finally heated to 80°C at 0.1 mm Hg pressure for 2 hours to remove volatiles.

Hydride replaced by alkyl functionality 86% (by ^{1}H NMR)

Analysis. (calculated for assuming 100% Si-H replacement, $C_{401}H_{1176}O_{194}Si_{186}$) C, 33.6 (33.5), H, 7.82 (7.75) %

^{1}H NMR. (ppm, $CDCl_3$) 0.08 (s, Si-CH_3), 0.91 (t, CH_3), 1.33 (m, CH_2), 1.51 (m, CH_2) 3.65 (t, O-CH_2)

IR (cm^{-1}) 2959, 2874, 1251, 1060, 843, 754

2.6.2 PREPARATION OF A 11 MOLE % n-BUTYL FUNCTIONALISED POLY(ORGANOSILOXANE) B2

This reaction was carried out as above using a (12%)-methylhydridosiloxane-(88%)-dimethysiloxane co-polymer (10.0g, 4.0mmoles) and n-butanol (1.19g, 16mmoles).

Hydride replaced by alkyl functionality 92% (by ^{1}H NMR)

Analysis (calculated assuming 100% replacement of Si-H, $C_{71}H_{204}O_{32}Si_{29}$)

Found C, 35.4 (35.6) ; H, 8.45 (8.52) %

^{1}H NMR. (ppm, $CDCl_3$) 0.08 (s, Si-CH_3), 0.91 (t, CH_3), 1.33 (m, CH_2), 1.51 (m, CH_2) 3.65 (t, O-CH_2)

IR (cm^{-1}) 2959, 2874, 1251, 1060, 843, 754

2.6.3 PREPARATION OF A 30 MOLE % n-BUTYL FUNCTIONALISED POLY(ORGANOSILOXANE) B3

This reaction was carried out as above using a (31%)-methylhydridosiloxane-(69%)-dimethylsiloxane co-polymer (10.0g, 4.8mmoles) and n-butanol (3.55g, 48mmoles).

Hydride replaced by alkyl functionality 96% (by ^{1}H NMR)

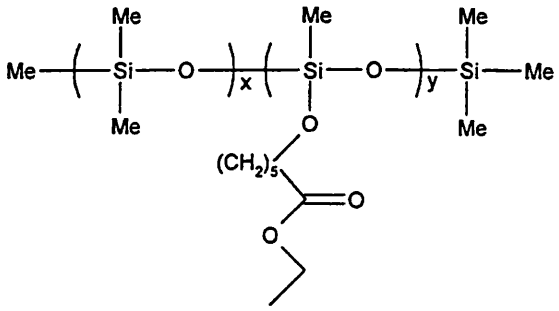
Analysis (calculated for assuming 100% Si-H replacement, $C_{87}H_{234}O_{37}Si_{29}$) C, 38.80 (38.93) ; H, 8.69 (8.72) %

^{1}H NMR. (ppm, $CDCl_3$) 0.08 (s, Si-CH_3), 0.91 (t, CH_3), 1.33 (m, CH_2), 1.51 (m, CH_2) 3.65 (m, CH_2) 3.65 (t, O-CH_2)

IR (cm^{-1}) 2959, 2874, 1251, 1060, 843, 754.

2.7 PREPARATION OF ETHYL ESTER FUNCTIONALISED LINEAR POLY(ORGANOSILOXANE) FLUIDS

One ester substituted poly(organosiloxane) was synthesised with the formula:



D1 30 mole % ester, X = 18, Y = 9

2.7.1 PREPARATION OF A 30 MOLE % ETHYL ESTER FUNCTIONALISED POLY(ORGANO)SILOXANE C3

(31%)-Methylhydrosiloxane-(69%)-dimethylsiloxane co-polymer (10.0g, 4.8mmol) was added to a flame dried 50cm^3 single necked flask fitted with a condenser. Ethyl 6-hydroxy-hexanate (0.56g, 48mmol) was treated with the catalyst dichloro(1,5-cyclooctadiene)platinum(II) (10mg, 2.67x10^{-5} moles) and then added to the siloxane in the flask. The reaction mixture was stirred and heated at 80°C under a nitrogen atmosphere for 24 hours. At this point a further 10mg of catalysis in ethyl-6-hydroxy-hexanate (0.1g, 0.6mmol) was added and heating continued for a further 72 hours at 80°C. The reaction mixture was then dissolved in 20cm^3 of dichloromethane filtered, and the dichloromethane removed using a rotary evaporator. The reaction mixture was finally heated to 95°C at 0.1 mm Hg pressure to remove volatiles.

Hydride replaced by ester functionality 96% (by ^{1}H NMR)

Analysis (calculated assuming 100% Si-H replacement, $C_{125}H_{288}O_{55}Si_{29}$)

Found C, 42.58 (42.71) ; H, 8.25 (8.33) %

^{1}H NMR (ppm, $CDCl_3$) 0.09 (s, Si-CH_3), 1.22 (t, CH_3), 1.34 (q, CH_2), 1.61 (m, $2CH_2$), 2.26 (CH_2-CO), 3.63 (t, O-CH_2), 4.10 (q, O-CH_2)

IR (cm^{-1}) 2959, 2870, 1740, 1458, 1373, 1251, 1161, 1059, 844.

2.8 PREPARATION OF DICHLORO(1,5-CYCLOOCTADIENE) PLATINUM(II)

The method used was based on that given by Drew[123] *et al* in the literature. Hydrated chloroplatinic acid (0.90g, 2.2mmol) was dissolved in glacial ethanoic acid (3.0cm^3, 52mmole) in a 50cm^3 Erlenmeyer flask giving a clear, orange solution. This solution was heated to 75°C and then treated with 1,5-cyclooctadiene (1.2cm^3, 2.2mmole) to afford a black, oily suspension. The reaction mixture was swirled gently and cooled to room temperature. Water (10cm^3) was added and the black suspension was stirred for one hour. The crude, grey product was collected an a Buchner funnel, and then washed with water (10cm^3) and diethyl ether (20cm^3). It was suspended in DCM (80cm^3) and the mixture boiled for five minutes. The solution was cooled, mixed with chromatograph-grade silica gel and the mixture allowed to settle. After filtration the residue was washed with two portions of DCM (10cm^3) to remove the pure product. The solvent was evaporated until the product started to crystallise and than the hot solution was poured into petroleum ether (b.p. 60-80°C) to precipitate a white solid. This was washed with petroleum ether (20cm^3) and dried.

Yield 0.20g (23%)

Analysis. (calculated for $C_8H_{12}PtCl_2$) Found C, 25.7 (25.7); H, 3.24 (3.23) %

^{1}H NMR (ppm, $CDCl_3$) 2.25 (4H, m, CH_2), 2.67 (4H, m, CH_2), 5.59 (4H, t, -CH=)

2.9 EXPERIMENTAL PROCEDURE

2.9.1 PREPARATION OF SUPPORTED LIQUID MEMBRANES

All the SLMs were produced using the same basic method. A circular pieces of Celgard of diameter 6 cm was placed in a Buchner funnel and water pump vacuum was applied. The functionalised poly(organosiloxane) which was to be encapsulated within the pores of the membrane was then poured evenly onto the Celgard and left for 5 min to allow the functionalised poly(organosiloxane) to penetrated into the pores. The membrane was then carefully removed from the Buchner funnel and excess poly(organosiloxane) allowed to drain away and the remainder wiped from the surface using a tissue. Two grades of Celgard were used. Their characteristics are shown in table 2.1.

Celgard	Pore size	Porosity	Thickness
K273	0.07 x 0.03 μm	33%	25 microns
2400	0.05 x 0.125 μm	38%	25 microns

Table 2.1 Celgard characteristics.

2.9.2 TEST SLM RIG

Each membrane was tested using a standard SLM rig. A schematic diagram of the test apparatus is shown figure 2.1.

The membrane disc was clamped between two PTFE rings in order to form a leak-free seal. The cells either side of the membrane were then filled with the feed and the stripping solution respectively using peristaltic pumps. Magnetic stirrers were placed against each end wall of the cells and were used to stir the magnetic fleas within the cells. The cells had a volume of 25 cm^3 each and the membrane area was 1.59 x 10^{-3} m^2.

Two types of run were carried out. The first was a batch run in which the pumps were switch off after the cells were filled and the solutions were stirred at a constant rate of 1000 rpm. After 12 hours the solutions in both sides were analysed in order to determine the concentration of the substrate transported through the membrane. The aim initially was to determine whether a particular poly(organosiloxane) can cause facilitated transport of the substrate.

If a positive result was achieved the second type of experiment, a dynamic continuous run, was carried out. In these a continuous flow of feed and stripping solution was passed though the cells at a flow rate of 1ml/min there was no re-circulation. The stripping solution was collected and the concentration of the substrate determined at 30 minutes intervals. From these results a steady state flux could be calculated.

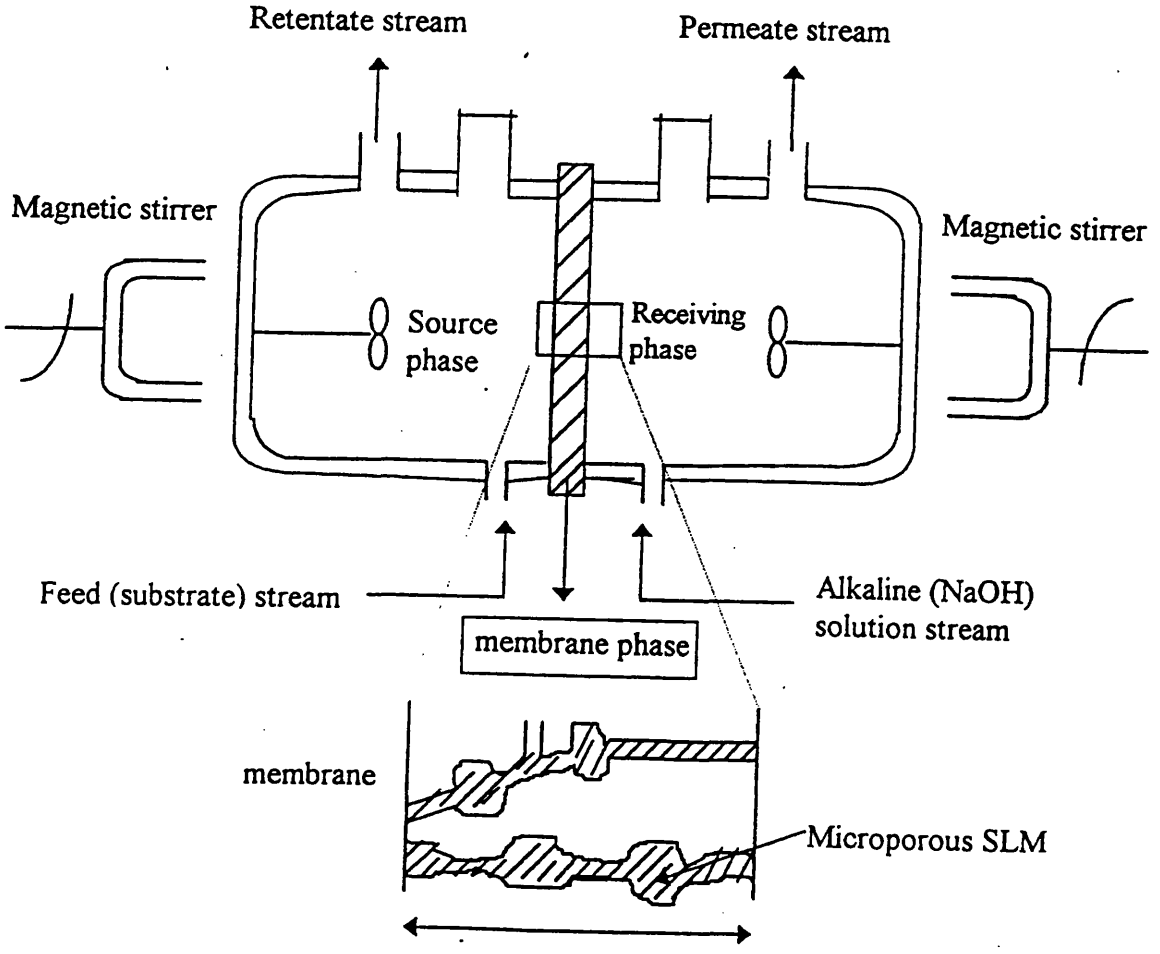


Figure 2.1 A schematic diagram of the test SLM rig

Two types of runs were carried out. The first was a batch run in which the pumps were switch off after the cells were filled and the solutions were stirred at a constant rate of 1000 rpm. After 12 hours the solutions in both sides were analysed in order to determine the concentration of the substrate transported through the membrane. The aim initially was to determine whether a particular poly(organosiloxane) can cause facilitated transport of the substrate.

If a positive result was achieved the second type of experiment, a dynamic continuous run, was carried out. In these a continuous flow of feed and stripping solution was passed though the cells at a flow rate of 1ml/min. The stripping solution was collected and the concentration of the substrate determined at 30 minutes intervals. From these results a steady state flux could be calculated.

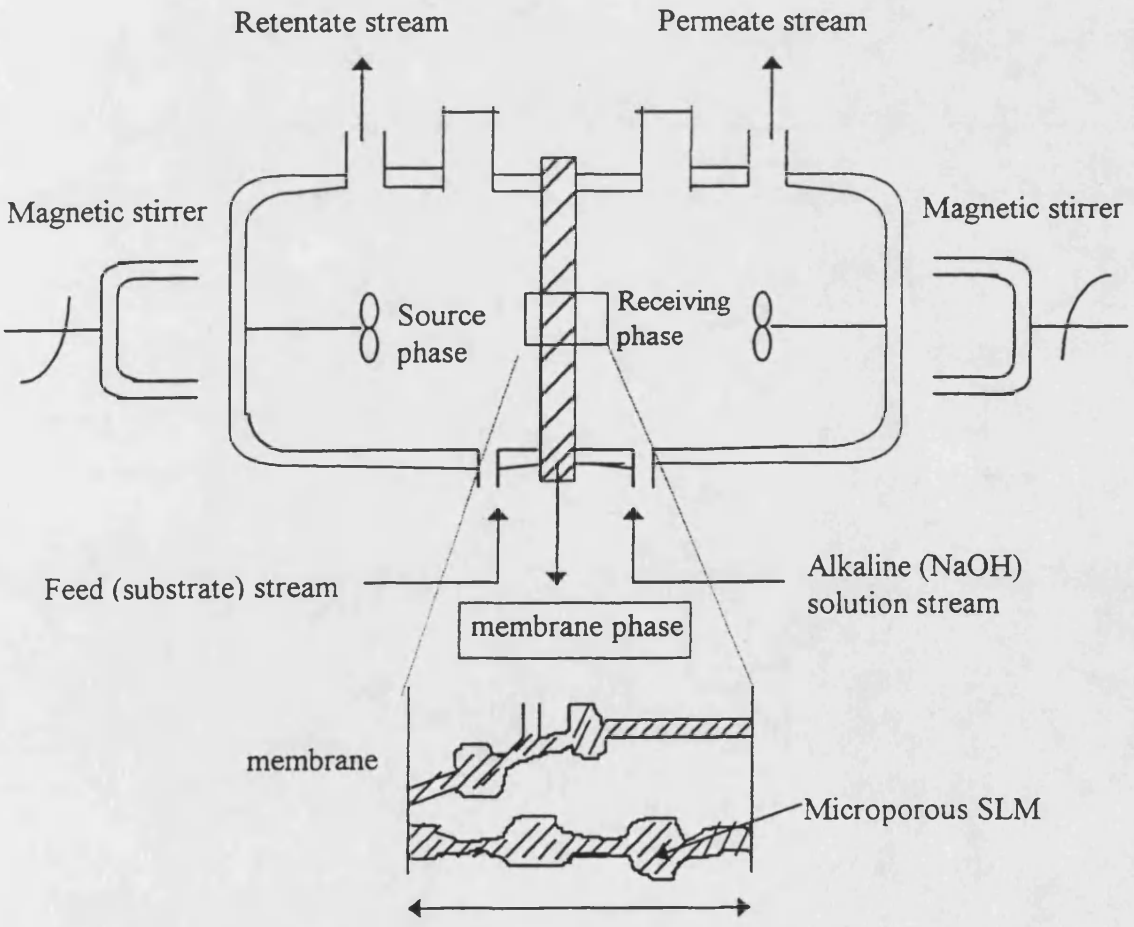


Figure 2.1 A schematic diagram of the test SLM rig

2.10 ANALYTICAL PROCEDURE

2.10.1 DETERMINATION OF PHENOL

Phenol was determined quantitatively using a Cecil 1020 ultra-violet spectrophotometer. Phenol absorb UV radiation with a very high absorption coefficient at 240 nm making determination of phenol by UV absorption a very sensitive technique in the absence of interfering aromatics. As phenol is a weak acid, it dissociates at high pH and hence at a given concentration UV absorption will be pH dependent. Thus the pH of each solution to be analysed was first adjusted to between pH 1-2 using dilute hydrochloric acid.

The spectrophotometer was calibrated at 240 nm by analysing a series of standard phenol solutions. A linear relationship between absorbance and concentration was noted at concentrations up to 300 ppm of phenol using a pure water blank.

2.10.2 DETERMINATION OF BENZYL ALCOHOL AND PHENOL DERIVATIVES

As with phenol, benzyl alcohol has an aromatic ring which will absorb UV radiation in accordance to Beer's law. The spectrophotometer was calibrated by analysing a series of standard benzyl alcohol solutions. Benzyl alcohol absorbed strongly at 240 nm and displayed a linear relationship between absorbance and concentration up to 200 ppm of benzyl alcohol. The samples to be analysed were diluted with distilled water to give a benzyl alcohol concentration between 10-200 ppm. The absorbance of the resultant solutions were then measured using a quartz cuvette with distilled water as the blank.

The phenol derivatives bromophenol, methoxyphenol and hydroquinone were all determined as for phenol above.

CHAPTER 3

SYNTHESIS OF ORGANOTRISILOXANE AND POLY(ORGANOSILOXANE) FLUIDS

3.0 SYNTHESIS OF ORGANOTRISILOXANES AND POLY(ORGANOSILOXANE) FLUIDS

3.1 INTRODUCTION

The synthesis of poly(organosiloxane) and trisiloxane fluids has normally been carried out by metal-catalysed hydrosilylation[112-114]. This method is high yielding and can be used to produce a wide range of poly(organosiloxane)s. A major problem associated with this method is the synthesis of the relevant alkenylated organic compounds needed for the addition to the polymer chain.

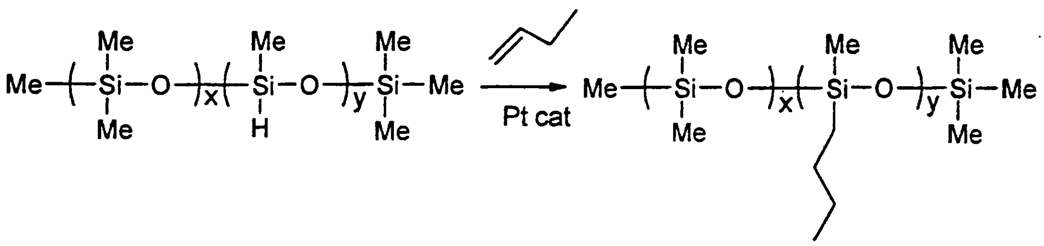


Figure 3.1 Hydrosilylation reaction of heptamethyltrisiloxane with a 1-alkene

In this project the synthesis of poly(organosiloxane)s was attempted using primary alcohols for attachment to various (dimethylsiloxane)-(methylhydridosiloxane) co-polymers. This type of reaction is widely used to crosslink poly(organosiloxane)s[119-122] but has not been widely reported for the synthesis of poly(organosiloxane) fluids. The major advantage of this method is the accessibility of -OH containing organic compounds which are in general easier to synthesis or purchase than alkenes. As hydrogen is evolved in this reaction, care must be taken if the reaction is carried out on anything other than a small scale.

$$Me_3Si(MeSiO(H))_x(Me_2SiO)_yOSiMe_3 + HOR \rightarrow Me_3Si(MeSi(OR)O)_x(Me_2SiO)_yOSiMe_3 + H_2$$

Equation 3.1 Reaction of an alcohol with a poly(dimethlysiloxane)-(methylhydridosiloxane) co-polymer.

3.2 SYNTHESIS OF ORGANOTRISILOXANES

The model siloxane heptamethyltrisiloxane was first used to determine the best reaction conditions for the synthesis of both the required organotrisiloxanes and the analogous poly(organosiloxane) fluids. Heptamethyltrisiloxane generally reacts in the same way as a (dimethylsiloxane)-(methylhydridosiloxane) co-polymer, but it exhibits reduced steric hindrance and the product can be purified by distillation and fully characterised using standard spectral and analytical techniques. This means that any addition reactions can be monitored more effectively than those involving the co-polymer.

3.2.1 CHOICE OF CATALYST

The reaction between primary alcohols and the Si-H residues in (dimethylsiloxane)-(methylhydridosiloxane) co-polymers is catalysts by organozinc[114] or organotin compounds, and especially by dibutyltin dilaurate[121-122] (see section 1.10.2), whereas in hydrosilylations platinum species are usually used as the catalyst (see section 1.10.1). To investigate whether platinum species would also catalyse H2 elemination, and also determine which catalyst would be most effective for the synthetic route shown in equation 3.2, three essentially identical reactions were carried out between 1,1,1,3,5,5,5-heptamethyltrisiloxane and 3-dimethylaminopropanol.

$$Me_3SiOMeSi(H)OSiMe_3 + HO(CH_2)_3NMe_2 \rightarrow Me_3SiOMeSi(O(CH_2)_3NMe_2)OSiMe_3 + H_2$$

Equation 3.2 Reaction of dimethylaminopropanol and heptamethyltrisiloxane

One reaction contained dibutyltin dilaurate (10mg, 1.58×10^{-5} moles) and the second dichloro(cyclooctadiene)platinum(II) (10mg, 2.67×10^{-5}moles). The third contained no catalyst. Each reaction mixture containing 4 mmol of the trisiloxane and dimethylaminopropanol was heated for 3 days at 80°C at which point an IR spectrum of

each was recorded. The reaction mixtures were then distilled under vacuum to remove unreacted starting materials and crosslinked trisiloxane. The yield of desired product is shown in table 3.1.

Catalyst used	% Yield of product
None	0
Dibutyltin dilaurate	10
Dichloro(1,5-cyclooctadiene)platinum(II) ($Cl_2PtC_8H_{12}$)	98

Table 3.1 % Yield of organofunctional trisiloxane using different metal catalysts.

The reaction which contained no catalyst produced none of the required product, and IR spectroscopy showed that the Si-H groups [2154 cm^{-1}] of the trisiloxane were still present at approximately the same intensity as at the start of the reaction.

Hydrogen was eliminated from the reaction mixture which contained dilbutyltin dilaurate as indicated by small gas bubbles in the reaction mixture after *ca* 2 hours at 80°C. After 3 days IR spectral analysis showed the reaction mixture contained no Si-H groups. The O-H absorption at 3300cm^{-1} appeared to be weaker than at the start. Distillation yield three fractions which were identified as unreacted dimethylamino propanol, a cross-linked siloxane containing no Si-H residues, and the required product respectively. A ^1H NMR spectrum confirmed the identity of the third fraction as the desired product, which was isolated in only 10% yield. On this evidence the dibutyltin dilaurate was ineffective as a catalyst under the reaction conditions used.

Hydrogen evolution was observed after *ca* 1hour at 80°C for the reaction mixture which contained the platinum catalyst. Infrared analysis after 3 days showed that all the Si-H groups had reacted, as had most of the OH groups of the alcohol. Vacuum distillation yield two fractions. The first fraction consisted of unreacted

dimethylaminopropanol, and the second was the required product. Its ^{1}H NMR spectrum is illustrated in figure 3.2. The yield of the product was 98% and there was no evidence of cross-linking of the siloxane. Thereafter all synthetic reactions carried out in this project utilised $Cl_2PtC_8H_{12}$ as the catalyst.

3.2.2 DIMETHYLAMINE FUNCTIONALISED ORGANOTRISILOXANE M1

The organotrisiloxane M1 was produced as a mobile colourless oil in 98% yield. Its IR spectrum showed absorptions at 1020, 866 cm^{-1} due to Si-O, as well as Si-Me vibrations at 1259 and 844 cm^{-1}.

The ^{1}H NMR spectrum in $CDCl_3$ showed a 21 proton singlet at δ 0.06 ppm arising from Si-Me moieties[124]. The spectrum also had a singlet corresponding to 6 protons at δ 2.1 ppm. This is assigned to the $N(CH_3)_2$ group, and has a chemical shift typical of N-Me containing compounds[125].

The ^{13}C NMR spectrum of M1 exhibited signals at 1.8 ppm ($Si-CH_3$) and at 45.5 ppm (NMe_2). Literature data for the amine carbon of a unprotonated tertiary amine[125] are *ca* 45.4 ppm. Data from ^{13}C NMR spectra of all the organotrisiloxane are given in table 3.2.

The ^{29}Si NMR spectra of all the organotrisiloxanes consist of two absorptions, one centred at *ca* 8 ppm and the other of lower intensity at *ca* -57 ppm. The signal at 8 ppm corresponds exactly to the literature value[126] for a Si with only one oxygen attached to it (e.g. Me_3Si-O). The peak at -57 ppm corresponds with the literature[127] data for a $MeSiO_3$ group.

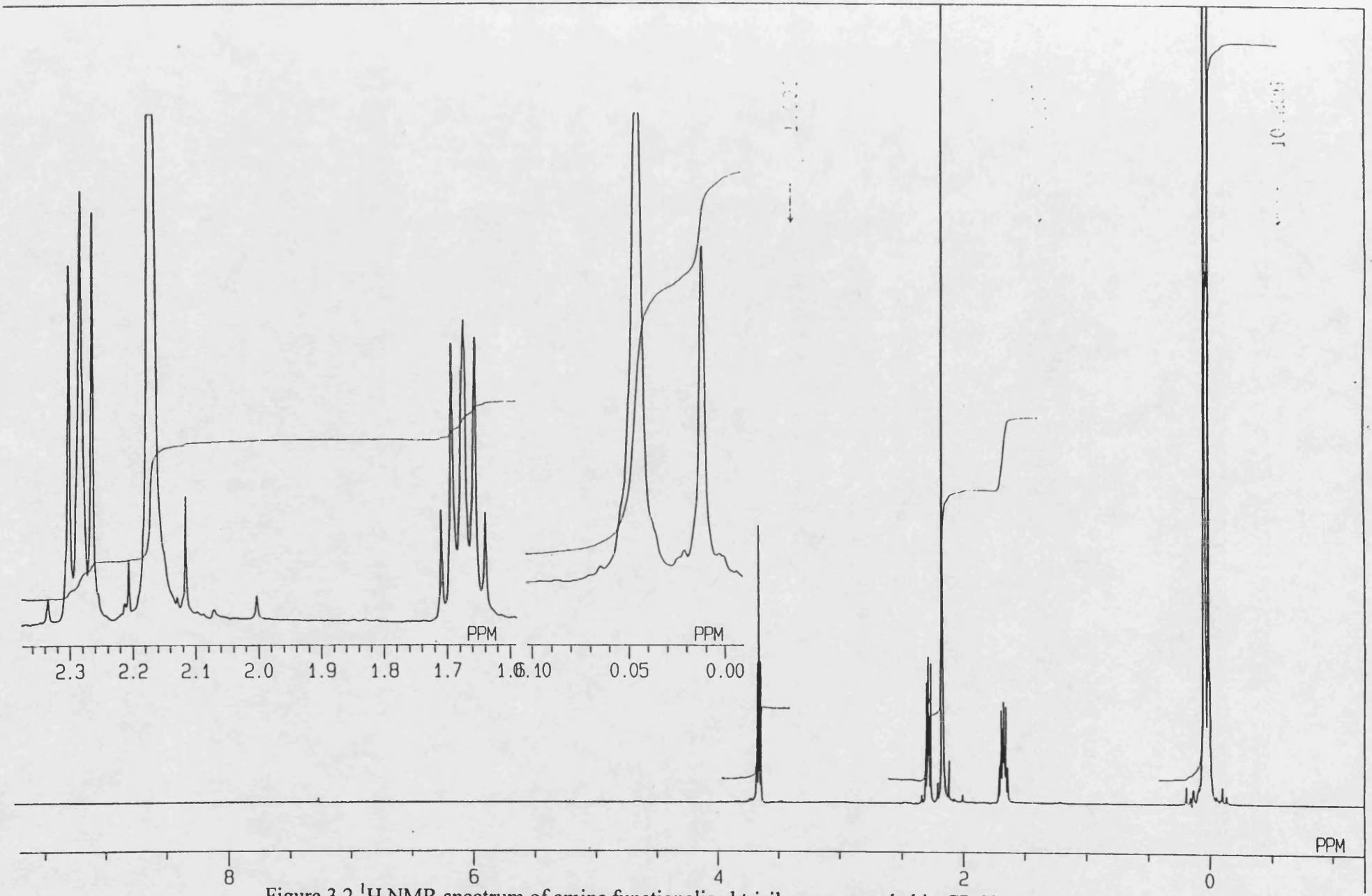


Figure 3.2 ^{1}H NMR spectrum of amine functionalised trisiloxane recorded in $CDCl_3$.

3.2.3 ETHYL ETHER FUNCTIONALISED ORGANOTRISILOXANE M2

The organotrisiloxane M2 was isolated as a mobile colourless oil in a yield of 95% following an analogous synthetic procedure to that given above. The IR spectrum of M2 had bands at 1064 cm^{-1} (Si-O vibration) and at 1251 and 844 cm^{-1} due to Si-CH_3 vibrations.

The ^1H NMR spectrum obtained in $CDCl_3$ contained a 21 proton singlet at δ 0.06 ppm arising from CH_3-Si groups of the siloxane[124] and two peaks assigned to CH_2-O (3.50, 3.79 ppm) and a signal at 1.20 ppm due to CH_3. The ^{13}C NMR spectrum exhibited 3 signals with chemical shifts appropriate for carbon singly bonded to oxygen[125]. Full details are given in table 3.2.

3.2.4 BUTYL FUNCTIONALISED ORGANOTRISILOXANE M3

The organotrisiloxane M3 was isolated in 94% yield as a colourless oil with a low viscosity. The IR spectrum had absorptions at 1060 cm^{-1} due to the Si-O vibration and bands at 1251 and 843 cm^{-1} due to Si-CH_3.

The ^1H NMR spectrum recorded in $CDCl_3$ contained a 21 proton singlet at 0.10 ppm corresponding to the CH_3-Si of the siloxane which is typically for methyl siloxanes[124], one signal at 3.65 ppm due CH_2-O, and three peaks assigned to the two CH_2 and one CH_3 residues. The ^{13}C NMR spectrum contained three bands in the region typical of C-C bonds[125] (10-50 ppm), and one signal at 62 ppm which is characteristic of C-O[125] (see table 3.2).

3.2.5 ETHYL ESTER FUNCTIONALISED ORGANOTRISILOXANE M4

The ester containing organotrisiloxane M4 was isolated as a low viscosity colourless oil in a yield of 95%. It had IR absorptions at 1059 cm^{-1} (Si-O) and at 1251, 844 cm^{-1} due to Si-CH_3. The C=O stretching mode was observed at 1740 cm^{-1}.

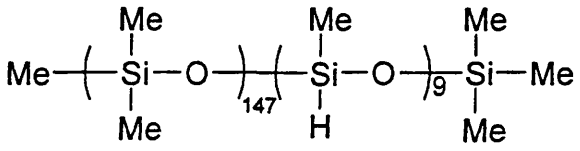
The ^{1}H NMR spectrum obtained in $CDCl_3$ exhibited a 21 proton singlet at δ 0.08 ppm assigned to SiMe groups[124], with three absorptions (2.27, 3.61, 4.01 ppm) assigned to hydrogens on a carbon adjacent to oxygen, and 3 signals due to the alkyl space chain. The ^{13}C NMR spectrum recorded in $CDCl_3$ exhibited 5 absorptions assignable to CH_2/CH_3 groups (10-50 ppm) and two in the CO region. The spectrum had one absorption at 173 ppm which is typically of C=O carbon[125]. The ^{13}C NMR data for each of the functionalised organotrisiloxane are summarised in table 3.2.

Compound	C_1	C_2	C_3	C_4	C_5	R	R
M1	62.3	58.6	31.8	-	-	45.5	-
M2	61.4	66.6	-	-	-	71.5	15.2
M3	61.9	34.6	19.0	13.9	-	-	-
M4	61.8	34.3	32.1	25.4	24.6	60.1	14.2

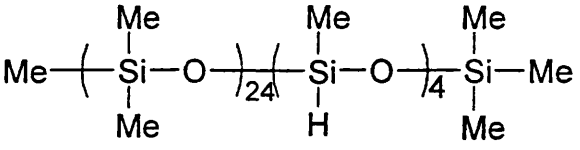
Table 3.2 ^{13}C NMR data for organotrisiloxanes M1-M4.

3.3 AMINE FUNCTIONALISED POLY(ORGANOSILOXANE)S

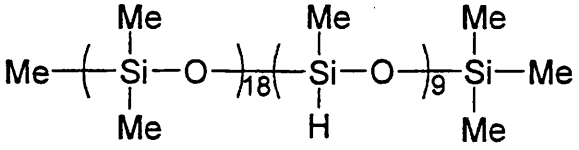
The co-polymers 5%-(methylhydridosiloxane)-95%-(dimethylsiloxane), 12%-(methylhydridosiloxane)-88%-(dimethylsiloxane), 31%-(methylhydridosiloxane)-69%-(dimethylsiloxane) were all analysed by ^{1}H NMR. From the data obtained, and their given average molecular weights (see below), the ratio of methylhydridosiloxane units and dimethylsiloxane units for each of the co-polymers could be determined with the results shown in figure 3.2.



5%-(methylhydridosiloxane)-95%-(dimethylsiloxane) co-polymer



12%-(methylhydridosiloxane)-88%-(dimethylsiloxane) co-polymer



31%-(methylhydridosiloxane)-69%-(dimethylsiloxane) co-polymer

Figure 3.2 Average compositions of the (methylhydridosiloxane)-(dimethylsiloxane) co-polymer starting materials.

To determine the degree of amine functionality incorporation, the intensity of the $SiMe_n$ signal in the proton NMR spectrum was compared with the intensity of the

signal of the NMe2 group and the ratio of theoretical intensity to actual intensity calculated. Measured NMR intensities were reproducible to 5%

Dimethyl amine containing siloxane	No. of SiMe hydrogens	Integral of Si-Me hydrogens (mm)	No. of NMe hydrogens assuming 100% Si-H reaction	Theoretical integral of NMe signal (mm)	Actual integral of NMe signal (mm)	% Si-H replacement
A1	1101	210	54	10	9	90 ± 5
A2	173	240	21	29	27	93 ± 5
A3	153	206	54	73	71	97± 5

Table 3.3 The degree of amine functionality loading of poly(organosiloxane)s A1-A3.

From the NMR results the dimethylamino fragment content for the polymers are: A1 4 mol %; A2 11 mol %; A3 30 mol %.

The elemental analyses in the experimental section 2.4 are quoted for a 100% theoretical yield. As is evident from table 3.3, the actual yields are a little lower than the theoretical yield. In table 3.4 the elemental analyses for nitrogen content are compared with those expected theoretically for both 100% and actual conversions.

Amine functionalised poly(organo siloxane)	Found % nitrogen	Calculated % nitrogen for 100% Si-H replacement	Calculated % nitrogen for the actual Si-H replacement (NMR)
4 mol % (A1)	0.67	0.88	0.79
11 mol % (A2)	1.90	1.96	1.81
30 mol % (A3)	4.40	4.47	4.34

Table 3.4 Found and calculated nitrogen contents for amine functionalised poly(organosiloxane)s.

As shown in table 3.4 the nitrogen content determined by microanalysis is in better agreement with the nitrogen content expected from NMR intensity measurements than the nitrogen content calculated for 100% Si-H replacement. As the ^{1}H NMR based determinations are estimated to be accurate to *ca* ± 5% for the percentage loading calculations, agreement between these two methods of determining functional group loading is good.

3.4 ETHYL ETHER FUNCTIONALISED POLY(ORGANOSILOXANE)S

The same method as given above was used to determine the ethyl ether loadings. The O-$(CH_2)_2$-O hydrogen signal intensities were used to determine the ether group content. Integral heights in table 4.5 are given in mm.

Ether Containing siloxane	No. of SiMe hydrogens	Integral of Si-Me hydrogens	No. of $(CH_2)_2$-O hydrogens assuming 100% Si-H reaction	Theoretical integral of $(CH_2)_2$-O signal	Actual integral of $(CH_2)_2$-O signal	% Si-H replacement
E1	1101	198	36	6	4	67 ± 5
E2	173	206	14	16.5	15	91 ± 5
E3	153	152	36	36	33.5	93 ± 5

Table 4.5 The degree of ether functionality loading of poly(organosiloxane)s E1-E3.

The ether content of the functionalised poly(organosiloxane)s E1,E2 and E3 are 4 mol %, 11 mol %, and 29 mol % respectively. As these poly(organosiloxane)s do not contain nitrogen, elemental analyses cannot be used to confirm these results, the change in percentage of carbon and hydrogen is relatively small over a large range of functional

group loadings. The mol % functionality for the E series of polymers are very similar to those of the amine functionalised series of poly(organosiloxane)s.

3.5 BUTYL FUNCTIONALISED POLY(ORGANOSILOXANE)S

A analogous NMR method was used to determine the degree of butyl functionalisation of the B series of poly(organosiloxane)s. The C-CH_3 hydrogen signals are used to determine the alkyl chain content as this is the most intense signal.

Alkyl Containing siloxane	No. of SiMe hydrogens	Integral of Si-Me hydrogens	No. of alkyl CH_3 hydrogens assuming 100% Si-H reaction	Theoretical integral of alkyl CH_3 signal	Actual integral of alkyl CH_3 signal	% Si-H replacement
B1	1101	220	27	5.5	5	91 ± 5
B2	173	215	10.5	13	12	92 ± 5
B3	153	225	27	39	36	92 ± 5

Table 4.6 The degree of alkyl functionality loading of poly(organosiloxane)s B1-B3.

From the results above the butyl content for the polymers are: B1 4 mol %, B2 11 mol %, B3 29 mol %. Elemental analyses cannot be used with confidence to confirm these results as the changes in percentage of carbon and hydrogen content would be slight for a significantly large range of alkyl group loadings.

3.6 ETHYL ESTER FUNCTIONALISED POLY(ORGANOSILOXANE)

Only one ethyl ester poly(organosiloxane) was produced using the 31%-(methylhydridosiloxane)-69%-(dimethylsiloxane) co-polymer as the starting siloxane material. The C-CH_3 hydrogen signal of the ester functionality has been used to estimate the ester content of the product. From the data in table 3.7, C3 has a 30 mol % ethyl ester content.

Ester Containing siloxane	No. of SiMe hydrogens	Integral of Si-Me hydrogens	No. of alkyl CH_3 hydrogens assuming 100% Si-H reaction	Theoretical integral of alkyl CH_3 signal	Actual integral of alkyl CH_3 signal	% Si-H replacement
C3	153	220	27	39	37.5	96 ± 5

Table 3.7 The degree of ester loading of poly(organosiloxane) C3.

CHAPTER 4

AMINE FUNCTIONALISED POLY(ORGANOSILOXANE) SLMs

4.0 AMINE FUNCTIONALISED POLY(ORGANOSILOXANE) SLMs

INTRODUCTION

In this chapter the results of experiments involving transport of a range of substrates through amine [-$(CH_2)_3NMe_2$] functionalised poly(organosiloxane) SLMs are described. The detailed investigations are centred on phenol (pK_a 9.89) as the test substrate. To determine the effect on transport of altering the substrate acidity without gross changes in substrate structure, other phenolic compounds were also investigated. These were hydroquinone, bromophenol and methoxyphenol, which have pK_a values of 10.35, 9.18 and 10.17 respectively. Two other substrates were also briefly investigated. These were benzyl alcohol, an aromatic alcohol which can be considered to be non-acidic, and phenoxyacetic acid, an aromatic carboxylic acid with a pK_a of 5.12, which represents a significantly stronger organic acid than the phenolic compounds.

The amine functional group was chosen as a carrier as it will complex with organic acids through acid/base interactions. Transport experiments were carried out using three amine functionalised poly(organosiloxane)s. These were A1 (4% amine), A2 (11% amine) and A3 (30% amine). Results were compared to those obtained using a pure PDMS SLM. Optimum conditions for the transport of phenol were first determined using the A2 functionalised fluid, and these same conditions were then applied to studies involving the use of A1 and A3. A discussion of other investigations on SLM mediated transport of phenol employing amine carriers[86-90] is given in section 1.6.1.

4.1 BATCH EXPERIMENTS WITH PHENOL AS THE TEST SUBSTRATE

In a batch process[128] the feed and stripping phases are continuously stirred at constant rate, and the substrate is allowed to equilibrate between the two phases. The aims of the experiments using pure PDMS and amine functionalised poly(organosiloxane) SLMs were to determine:-

i) If phenol is transported across a pure PDMS SLM membrane with and without an applied pH gradient.

ii) If an amine functionalised poly(organosiloxane) SLM could transport phenol against a concentration gradient using a pH gradient as the driving force.

iii) The effect of changing the amine functional group loading on the transport properties of poly(organosiloxane) SLMs.

4.1.1 TRANSPORT OF PHENOL THROUGH A PDMS SLM

In these experiments the stripping phase was distilled water, the feed phase contained a phenol concentration within the range 15,000 to 35,000 ppm. No applied pH gradient was used but a small pH gradient exists at the start of each run as the pH of the phenol feed is *ca* 5 and that of the stripping phase is initially *ca* 7. After a very short time the pHs of both phases will essentially equalise, due to phenol entering the stripping phase and reducing the pH to *ca* 5.

The concentration of phenol in the stripping phase was calculated at the steady state, which is know from previous experiments to be reached within 12 hours (section 4.1.2.1). The results of batch studies on PDMS fluids are shown in table 4.1.

Initial phenol feed phase conc. (ppm)	% Phenol extracted into the stripping phase at steady state
15,000	50 ±2
25,000	50 ±2
35,000	50 ±2

Table 4.1 Percentage phenol extracted using PDMS SLMs and a distilled water stripping phase.

These results show that phenol is transported across a PDMS SLM, and that Ficks first law of diffusion is obeyed when a concentration gradient provides the only driving force.

The batch experiments were repeated using a stripping phase of 1.0M NaOH. The pH gradient produces a driving force across the SLMs which can reinforce or oppose the phenol concentration gradient. As phenol is a weak acid, under the conditions of the experiments it will be over 99% in the ionised form on the basic side of the membrane, and over 99% in the unionised form on the feed side. Thus a concentration gradient of unionised phenol can be created across the membrane even if the total phenol concentration gradient opposes it, providing the phenate ion is transported across the membrane much less readily than molecular phenol.

$$[PhOH]_{aq} \quad \leftrightarrow \quad [PhO^-]_{aq} + [H^+]_{aq}$$

Initial feed phase phenol conc. (ppm)	% Phenol extracted into the stripping phase at steady state
15,000	65 ±2
25,000	66 ±2
35,000	64 ±2

Table 4.2 Percentage phenol extracted using PDMS SLMs and 1.0M NaOH stripping phase.

These results clearly show that phenol can be transported through a PDMS membrane against a concentration gradient if a pH gradient is applied across the membrane. This observation can be related to differences anticipated in the solubility and diffusivity of the unionised phenol, compared with the phenate ion, in a fluid poly(dimethylsiloxane). Thus the flux through the membrane of unionised phenol at any given concentration is higher than the flux of the phenate ion at the same concentration, so at steady state the stripping phase contains a higher concentration of phenol than the

feed phase. Over the phenol concentration range of 15,000-35,000 ppm the percentage phenol transported across the membrane is constant within the limits of measurements.

4.1.2 BATCH EXPERIMENTS WITH AN A2 FUNCTIONALISED POLY(ORGANOSILOXANE) SLM

The optimum conditions for batch studies were determined using the A2 functionalised poly(organosiloxane). Experimental conditions which were varied and their effects assessed were:

i) The period of time over which the batch runs were carried out.
ii) The NaOH concentration in the stripping phase.
iii) The pH of the feed phase.

4.1.2.1 STEADY STATE IN THE BATCH PROCESS

Steady state in a batch process occurs when equilibrium is reached. At this point the rate of transport of phenol across the membrane is the same in both directions. This was first determined for membrane A2 using a feed phase containing 15,000 ppm of phenol, and a stripping phase of 1M NaOH. Runs were stopped at different time intervals and the phenol concentration in the stripping phase was determined. The results are shown in figure 4.1.

After *ca* 12 hours equilibrium had been reached. All subsequent batch runs on all membrane materials were also carried out over a 12 hour period. The time to reach steady state is considerably longer in this system than in conventional SLM systems[80,87] the majority of which reach steady state within 2 hours. This is probable due to the relatively high viscosity of the amine functionalised poly(organosiloxane) compared to the solvent/carrier systems in conventional SLMs.

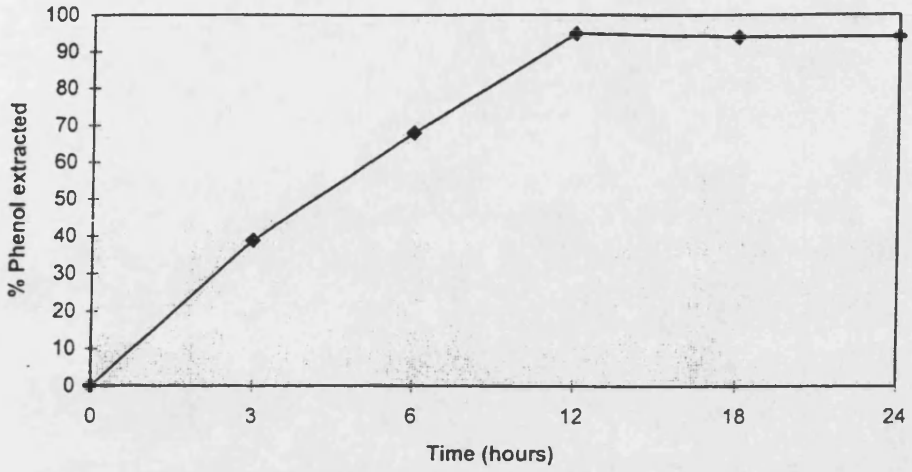


Figure 4.1 Percentage of phenol extracted as a function of time using an A2 SLM.

4.1.2.2 THE EFFECT OF NaOH CONCENTRATION IN THE STRIPPING PHASE ON THE TRANSPORT OF PHENOL

In this experiment a pH gradient was used to create the principle driving force. Consequently the concentration of NaOH within the stripping phase which gives the highest steady state phenol concentration was determined. NaOH concentrations in the stripping phase were varied in the range 0-2M.

Phenol conc. (ppm)	Distilled water as stripping phase (% phenol)	0.1M NaOH as stripping phase (% phenol)	0.2M NaOH as stripping phase (% phenol)	1.0M NaOH as stripping phase (% phenol)	2.0M NaOH as stripping phase (% phenol)
15,000	50 ±2	86 ±2	85 ±2	93 ±2	92 ±2
25,000	50 ±2	64 ±2	75 ±2	94 ±2	94 ±2
35,000	49 ±2	64 ±2	73 ±2	96 ±2	95 ±2

Table 4.3 Percentage of phenol transported into the stripping phase consisting of different concentrations of NaOH.

When distilled water was used as the stripping phase no significant pH gradient existed across the membrane once transportation had started, and at equilibrium *ca* 50% of phenol had been transferred into the stripping phase, in accord with Ficks first law of diffusion.

When 0.1M NaOH was used as the stripping phase, with an initial phenol concentration of 15,000 ppm in the feed phase, 85% of the phenol was extracted at equilibrium. The percentage phenol extracted decreased to 64% on increasing the initial phenol feed concentration to 25,000 ppm and then to 35,000 ppm. The percentage phenol extracted increased at higher phenol feed concentration on using 0.2M NaOH rather than 0.1M NaOH as the stripping phase. At high NaOH concentrations (1.0; 2.0 M) the stripping phases all contained *ca* 94% of the available phenol. This indicates that NaOH concentration is a limiting factor below 1.0M. Thus 0.2M NaOH solution contains only 8,000 ppm of NaOH and the phenol concentration in the stripping phase is over 20,000 ppm at equilibrium for the run with an initial phenol feed phase concentration of 35,000 ppm. Although phenol is only a weak acid its large concentration dramatically reduces the pH of the stripping phase from *ca* 13 to *ca* 10 (see table 4.4).

A 1.0M NaOH solution has a NaOH concentration of 40,000 ppm, which exceeds that of the phenol in the stripping phase under any of the experimental conditions. Thus the pH differential across the membrane is not significantly affected (see table 4.4). Complete extraction of the phenol was not achieved in any of the experiments. This is probable due to phenate ion slowly back diffusing through the poly(organosiloxane). Studies carried out previously at Bath[129] have shown that charged species (including OH^-) do diffuse though PDMS, but that their rate of diffusion is low compared with that of uncharged species of a similar size and type. In this study we confirmed in separate experiments that transportation of the phenate ion between alkaline feed and alkaline stripping phases occurs with a flux of *ca* 2 g/hour/m^{-2} using an initial phenol feed concentration of 30,000 ppm.

Initial phenol feed conc. (ppm)	0.1M NaOH stripping phase	0.2M NaOH stripping phase	1.0M NaOH stripping phase
15,000	10.1 ± 0.2	10.1 ± 0.2	13.1 ± 0.2
25,000	10.0 ± 0.2	10.2 ± 0.2	13.5 ± 0.2
35,000	9.8 ± 0.2	10.4 ± 0.2	13.1 ± 0.2

Table 4.4 pH of the stripping phases at steady state for each of the batch runs.

From results obtained using stripping phases containing low NaOH concentrations it is apparent that the reduction in the pH is sufficient to allow phenol within the stripping phase to be present in significant quantities in both the ionised and unionised form. Thus unionised phenol in this phase will diffuse back to the feed phase, and the concentration of unionised phenol at steady state will tend to equalise in both the phases.

The pH at which essentially all phenol is in the form of the phenate ion can be calculated using equation 4.1.

$$pH = \tfrac{1}{2}pK_a + \tfrac{1}{2}pK_w + \tfrac{1}{2}\log_{10} S \qquad \text{Equation 4.1}$$

pK_a of phenol = 9.89, pK_w = 14.0, S (concentration of phenol) = 0.35 mol l^{-1}

Thus at pHs greater than 12.5, over 99.9% of the phenol is in the ionised form. At steady state when using 1M or 2M NaOH as the stripping phase, the phenol is effectively entirely in the form of phenate ions. Stripping phases which initially contained 0.1 and 0.2M NaOH had a final pH of *ca* 10 at steady state and so both phenate ion (PhO^-) and unionised (PhOH) will be present in a ratio which can be calculated from equation 4.2.

$$Phenol_{\text{-nonionised}} / phenol_{total} = 1 / [1 + 10^{(pH-pKa)}] \qquad \text{Equation 4.2}$$

At a pH of 10.1, 45% of the phenol is in the unionised form. The concentration of unionised phenol in the stripping phase at steady state can now be calculated and compared with the unionised phenol concentration in the feed phase at steady state. These results are shown in table 4.5.

0.1M NaOH

Initial feed phenol conc. (ppm)	Steady state conc. of PhOH in the feed phase (ppm)	Steady state conc. of PhOH in the stripping phase (ppm)
15,000	2,100 ± 2%	5,800 ± 12%
25,000	9,000 ± 2%	7,200 ± 12%
35,000	12,600 ± 2%	11,500 ± 12%

0.2M NaOH

Initial feed phenol conc. (ppm)	Steady state conc. of PhOH in the feed phase (ppm)	Steady state conc. of PhOH in the stripping phase (ppm)
15,000	2,300 ± 2%	5,700 ± 12%
25,000	6,300 ± 2%	8,000 ± 12%
35,000	9,500 ± 2%	10,200 ±12%

Table 4.5 Concentration of unionised phenol at steady state in the feed and stripping phases.

The uncertainty in the PhOH concentration within the feed phase as determined by UV spectrophotometry is approximately ± 2%. The uncertainty in calculating the PhOH concentration from pH measurements in the stripping phase is ± 12%. This large value arises from the similarity in the pHs of the stripping phases and the pK_a of phenol (9.89). Small uncertainties in the experimental pH measurements have a dramatic effect on the calculated PhOH concentration in a given stripping phase. The results in table 4.5 show that with initial phenol concentrations of 25,000 or 35,000 ppm the concentrations

of unionised phenol at steady state in the feed and stripping phases consisting of 0.1M or 0.2M NaOH are very similar. At the lowest initial phenol concentration of 15,000 ppm, the unionised phenol concentrations in the stripping and feed phases at steady state are significantly different. The reasons for this are not obvious.

4.1.2.3 EFFECT OF pH OF THE FEED SOLUTION ON THE TRANSPORT OF PHENOL

Batch experiments were carried out under the same conditions as in 4.1.2.2 but using a feed phase consisting of phenol dissolved in 0.1M hydrochloric acid, in order to assess the effect of lowing the feed phase pH on the extraction of phenol.

Phenol conc. (ppm)	Feed phase distilled water, stripping phase 1.0M NaOH (% phenol)	Feed phase 0.1M HCl, stripping phase 0.1M NaOH (% phenol)	Feed phase 0.1M HCl, stripping phase 0.2M NaOH (% phenol)	Feed phase 0.1M HCl, stripping phase 1M NaOH (% phenol)
15,000	93 ± 2	85 ± 2	85 ± 2	93 ± 2
25,000	94 ± 2	64 ± 2	78 ± 2	92 ± 2
35,000	96 ± 2	62 ± 2	80 ± 2	93 ± 2

Table 4.6 The percentage of phenol extracted using a feed phase containing 0.1M HCl.

If the data in tables 4.3 and 4.6 are compared it becomes clear that the addition of HCl has made little difference to the amount of phenol extracted. The pH of the distilled water/phenol feed phase is 5.5 ± 0.2 compared with 1.1 ± 0.2 for the HCl/phenol feed phases. This shows that the magnitude of the pH gradient across the membrane does not effect the amount of phenol extracted over a feed phase pH range of 1-5.The pH of the distilled water/phenol feed phase at the end of a batch runs was 8.0 ±

0.2 (table 4.7). The increase in pH is due to the reduction in the phenol concentration within the feed phase and the simultaneous diffusion of OH^- from the stripping phase into the feed phase.

Phenol conc. (ppm)	Feed phase distilled water, stripping phase 1M NaOH	Feed phase 0.1M HCl, stripping phase 0.1M NaOH	Feed phase 0.1M HCl, stripping phase 0.2M NaOH	Feed phase 0.1M HCl, stripping phase 1M NaOH
15,000	7.9 ± 0.2	1.1 ± 0.2	1.2 ± 0.2	1.1 ± 0.2
25,000	8.0 ± 0.2	1.2 ± 0.2	1.2 ± 0.2	1.1 ± 0.2
35,000	7.8 ± 0.2	1.3 ± 0.2	1.2 ± 0.2	1.2 ± 0.2

Table 4.7 pH of the feed phase after each batch run.

As noted earlier, a small change in pH is unlikely to effect significantly the concentration of unionised phenol. Thus at pH 5 over 99.9% of the phenol is in the unionised form so increasing acidity will affect this figure only very slightly. The effect of pH on the amine functionality is deferred until later. At pH 8 *ca* 98% of the phenol is in the unionised form, and this slight decrease is not significant either.

The results from the amine functionalised poly(organosiloxane) membranes can be compared with those reported in the literature for other amine carrier[87-90] systems used to transport phenol. In a study of the transport of phenol using tertiary octamine (TOA) carriers[87] the highest fluxes were shown to occur for a feed phase at a pH *ca* 1. This was achieved by the addition of sulphuric acid to the feed solution. The TOA reacts with the sulphuric acid to form $TOAH_2SO_4$, which is more effective in the facilitated transport of phenol than the free amine (see 1.6.1). This contrasts with our studies on amine functionalised poly(organosiloxane)s in which the feed phase pH does not effect the extraction of phenol between the pH limits 1-8.

4.1.3 EFFECT OF THE AMINE FUNCTIONAL GROUP CONCENTRATION ON PHENOL EXTRACTION

Investigations were carried out on the effect on phenol extraction of increasing the amine functional group loadings in the poly(organosiloxane) membranes. The stripping phase was 1.0M NaOH. Data on phenol extraction for the three loadings are given in table 4.8.

Phenol conc. (ppm)	PDMS (% phenol)	A1 (4% amine) (% phenol)	A2 (11% amine) (% phenol)	A3 (30% amine) (% phenol)
15,000	65 ± 2	80 ± 2	92 ± 2	93 ± 2
25,000	66 ± 2	79 ± 2	94 ± 2	98 ± 2
35,000	64 ± 2	80 ± 2	96 ± 2	99 ± 2

Table 4.8 Percentage of phenol extracted using different loadings of functionalised amine poly(organosiloxane).

A1 (4% amine loading) SLMs extracted *ca* 80% phenol at steady state compared with 65% extraction for PDMS membranes. Thus the amine group has a significant effect on phenol extraction even at low concentration. The A2 and A3 membranes gave percentage extractions of *ca* 94% and 97% respectively. As phenate ions slowly back diffuse through the amine functionalised poly(organosiloxane) SLMs, 100% phenol extraction is not expected.

It has been reported that *ca* 95% extraction of phenol can be achieved using decanol[80], polyglycol[98], and amine carrier[90] based conventional SLMs. This figure is comparable with that achieved using moderately loaded amine functionalised poly(organosiloxane) SLMs.

4.2 DYNAMIC CONTINUOUS FLOW RUNS

The batch runs showed that phenol can be transported against a concentration gradient using an amine functionalised poly(organosiloxane) SLM with a pH gradient driving force. The experimental evidence indicated that the transport process was controlled primarily by the different solubilities and/or diffusitities of phenol and the phenate ion in the polymer membrane. There was little conclusive evidence of facilitated transport. It is possible that the amine functionality is acting as a carrier but that this effect is small in comparison with the much larger solubility effects. To investigate this possibility further, continuous flow studies were carried out.

In the continuous flow runs the stripping and feed phases were pumped continuously through their respective cells at a flow rate of 1ml/min unless otherwise stated. Under these conditions steady state fluxes were calculated. In a SLM there are five discreet steps to be considered (section 1.2.1) and steady state is reached when any one of these steps becomes limiting. The flux of the substrate in this limiting step is then the steady state flux. Changing the conditions can affect the limiting step in the transport mechanism, so having a significant effect on the steady state flux. In order to investigate the transport mechanism, conditions such as pH and amine loading were varied and the effect on the steady state flux determined. From this information an understanding of the transport mechanism was gained.

4.2.1 CONTINUOUS FLOW EXPERIMENTS USING AN 11% AMINE FUNCTIONALISED POLY(ORGANOSILOXANE)

An 11% amine functionalised poly(organosiloxane) was chosen as the liquid membrane material upon which all primary investigations were carried out in order to determine the optimum conditions for continuous flow studies. This material had also been used to optimise conditions in batch experiments.

The experimental conditions which were varied and their effects assessed were:-

i) The NaOH concentration in the stripping phase.
ii) The pH of the feed phase.
iii) The flow rates of stripping and feed phases.
iv) The stripping and feed phase stirring rates.

4.2.1.1 THE EFFECT OF PHENOL FEED CONCENTRATION ON PHENOL FLUX USING 11% AMINE FUNCTIONALISED POLY(ORGANOSILOXANE)

The first run was carried out using a feed phase concentration of 5,000 ppm phenol with the stripping phase consisting of 0.1M NaOH. The flow rate of 1ml/min^{-1} was used in this and all subsequent runs unless stated otherwise. The initial aim was to determine the time taken for the system to attain equilibrium.

Data in figure 4.2 show that the concentration of phenol in the stripping phase increases rapidly for 1.5 hours, and it then becomes approximately constant at *ca* 1,000 ppm. This corresponds to 20% extraction. Under these conditions the pH of the stripping phase containing phenol is slightly lower than the initial pH but the change does not have any significant affect on the equilibrium between the phenol and phenate ion within the stripping phase. Runs were next carried under the same condition as above but with phenol feed concentrations ranging from 500 to 35,000 ppm. The results are summarised in table 4. 9.

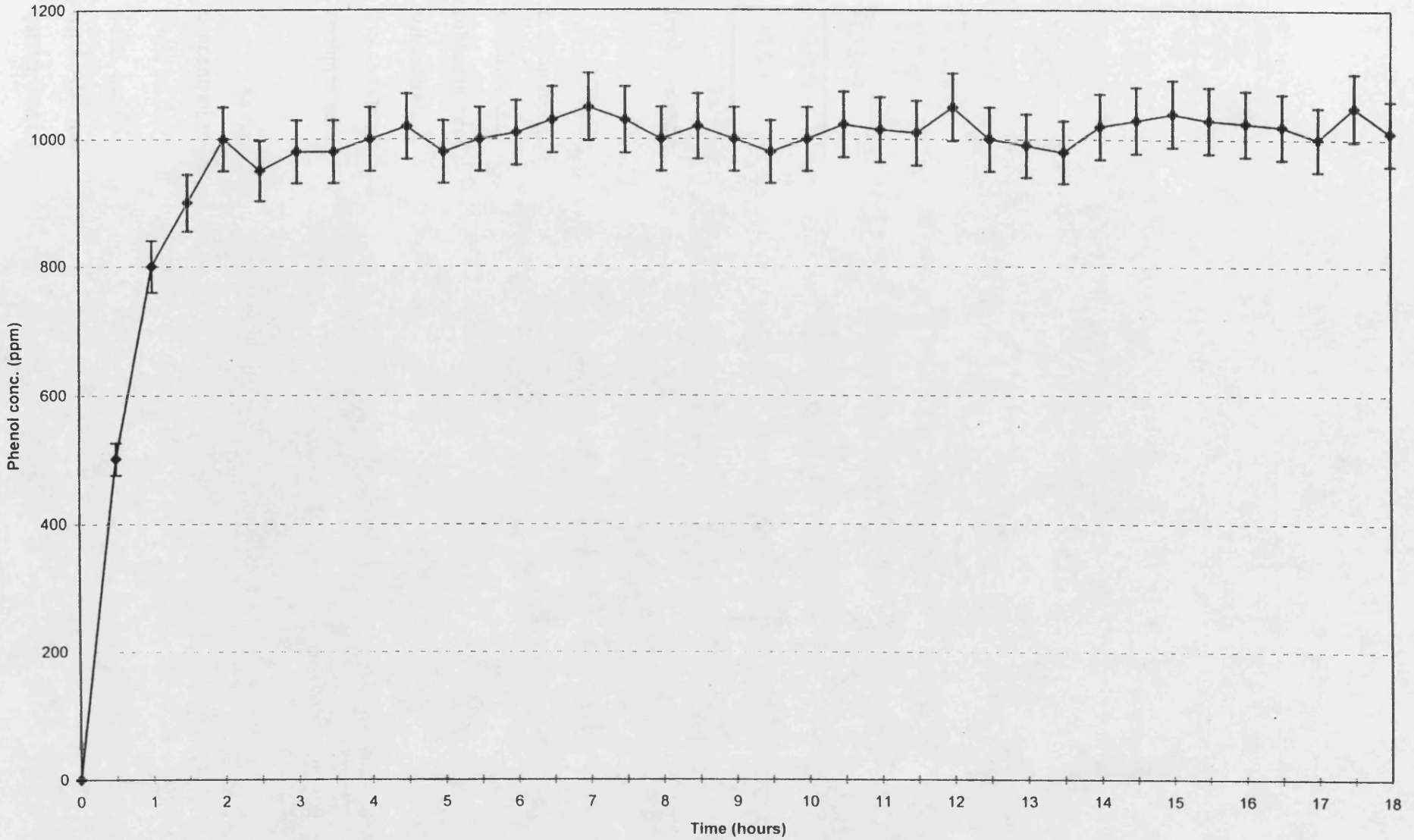


Figure 4.2 Concentration of phenol in the stripping phase against time.

Initial phenol feed phase conc. (ppm)	Steady state conc. (ppm)	Flux (g/hour/m^{-2})
500	90 ± 2%	4
1,000	180 ± 2%	81
2,500	560 ± 2%	20
5,000	1,000 ± 2%	40
10,000	1,800 ± 2%	70
15,000	2,610 ± 2%	98
20,000	3,300 ± 2%	122
25,000	3,650 ± 2%	140
30,000	4,300 ± 2%	160
35,000	4,800 ± 2%	181

Table 4.9 Flux and steady state concentration of phenol for a range of phenol feed concentrations.

The concentration differential across the membrane provides an important driving force for the permeation of a substrate. In a SLM containing a carrier the substrate flux is expected to be directly proportional[29] to the feed concentration of the substrate, provided the substrate concentration is low with respect to the carrier concentration. At high substrate concentration with respect to carrier concentration, the flux is expected to become independent of the substrate concentration, as the carrier becomes saturated with substrate.

As can be seen from table 4.9 the phenol fluxes are dependant on phenol feed concentration over the whole range of concentrations used in this investigation. This could be due to the fact that the feed concentration has not reached carrier saturation point, but this is unlikely due to the very wide phenol concentration range that has been used. Alternatively the phenol fluxes in table 4.9 could result from a combination of a carrier facilitated transport mechanism together with phenol diffusion resulting from the

concentration gradient. The flux attributable to each component through these amine functionalised poly(organosiloxane) SLMs needs to be clarified.

4.2.1.2 PRECISION OF THE FLUX MEASUREMENTS

It has been shown (see section 2.3.1) that calculating the phenol concentration spectrophotometrically has a precision of ± 2%. The values of the phenol flux reported will have a lower precision than this, due to inherent fluctuations of various controls within the test rig system including the flow rate. It is important to know the reproducibility and limitations of the flux measurements. These were investigated by repeating runs (normally three times) at given concentrations and analysing the results.

Initial feed phase phenol conc. (ppm)	Flux (g/hour/m^{-2}) Result 1	Flux (g/hour/m^{-2}) Result 2	Flux (g/hour/m^{-2}) Result 3
1,000	7	8	8
2,500	20	22	20
5,000	40	35	38
10,000	70	68	72
15,000	98	88	95
20,000	121	125	123
25,000	140	140	145
30,000	155	163	160

Table 4.10 Phenol fluxes for a range of phenol feed concentrations.

The results show that the degree of precision in the flux measurements is directly related to the phenol feed concentration. At phenol feed concentrations < 10,00 ppm the precision in the flux measurement is *ca* ± 5% but it is only *ca* ± 2% at higher concentration This latter value is within the precision of measuring phenol concentration by UV spectrophotometer.

A value of ± 5 g/hour/m^{-2} has been taken as the precision for systems with a feed phenol concentration of over 10,000 ppm, and ± 3 g/hour/m^{-2} for phenol concentrations of under 10,000 ppm. This is the largest difference between any two flux values at the same phenol feed concentration, with the majority of flux values showing a smaller variation.

4.2.1.3 THE EFFECT OF PHENOL FEED CONCENTRATION ON PHENOL FLUX THROUGH PDMS

The results from the experiments in which different phenol feed concentrations were employed in conjunction with membrane material A2 indicated that two different transport mechanisms may be occurring. The first involves phenol diffusing through the membrane under a concentration gradient driving force, and the second involves facilitated transport with the amine functionality acting as the carrier. An investigation was carried out using pure PDMS SLMs to determine the non-facilitated flux. Experimental runs were carried out under the same conditions as given in 4.2.1.1, and the results obtained are shown in table 4.11.

Phenol feed conc. (PPM)	Flux (g/hour/m^{-2})
500	2 ± 3
1,000	3 ± 3
2,500	8 ± 3
5,000	13 ± 3
10,000	26 ± 5
15,000	35 ± 5
20,000	46 ± 5
25,000	60 ± 5
30,000	71 ± 5

Table 4.11 Phenol fluxes through PDMS with different phenol feed concentrations.

The results show that phenol fluxes through PDMS are considerably lower than those obtained using the amine functionalised poly(organosiloxane) membrane, A2. Thus the functional group has a significant effect on the transport of phenol. This may be facilitation effect, or it may result from an increased inherent solubility of phenol in the amine functionalised poly(organosiloxane). The results from the batch experiments (see section 4.1) indicate that phenol does indeed have a greater solubility in amine functionalised poly(organosiloxane)s than in PDMS. Therefore it is likely that at least some of the increase in phenol fluxes are due to the solubility effects.

4.2.1.4 EFFECT OF ALTERING FLOW RATES ON PHENOL FLUXES

Facilitated transport of a substrate involves the 5 steps shown below, any one of which may be rate determining. Flow rate was varied in order to investigate which step is limiting.

i) Substrate diffuses through the boundary layer.
ii) The substrate complexes with the carrier at the membrane/feed phase interface.
iii) The substrate/carrier complex diffuses through the membrane.
iv) The substrate de-complexes at the membrane/feed interface and enters the stripping phase.
v) The substrate diffuses through the boundary layer of the stripping phase.

Increasing the flow rate has two main effects. Firstly it reduces the boundary layer thickness by increasing the turbulence. Secondly it reduces the retention time of the substrate within the system, which can have a effect on the complexation/de-complexation steps if these steps are slow.

Flow rate of feed phase (ml/min^{-1})	Flow rate of stripping phase (ml/min^{-1})	Initial phenol feed phase conc. (ppm)	Flux ($g/hour/m^{-2}$)
1.0	1.0	1,000	8 ± 3
2.0	1.0	1,000	8 ± 3
0.5	0.5	1,000	7 ± 3
1.0	2.0	1,000	7 ± 3
1.0	1.0	5,000	40 ± 3
0.5	0.5	5,000	35 ± 3
2.0	1.0	5,000	42 ± 3
1.0	2.0	5,000	38 ± 3
1.0	1.0	20,000	122 ± 5
2.0	1.0	20,000	125 ± 5
1.0	2.0	20,000	118 ± 5
0.5	0.5	20,000	120 ± 5

Table 4.12 Fluxes at different flow rates and feed phenol concentrations.

The fluxes at any given phenol feed concentration are only slightly affected by changes in flow rates. The differences between the fluxes are all within the limits of the analytical measurements so it is not possible to infer any definite conclusions, but the results indicate two possible trends. Firstly, that the phenol fluxes from runs with a flow rate of $0.5ml/min^{-1}$ on both sides of the membrane are lower than analogous runs with flow rates of $1ml/min^{-1}$ on both sides of the membrane. This may be caused by changes in the boundary layer. The second trend is that the phenol fluxes are lower for runs with a stripping phase flow rate of $2ml/min^{-1}$ compared to the analogous runs with a flow rate of $1ml/min^{-1}$. This indicates that the phenol de-complexation step on the stripping phase is probably a relatively slow process.

4.2.1.5 EFFECT OF STIRRING RATE ON PHENOL FLUXES

The stirring rate may also affect the flux due to changes in boundary layer effects. If transport through the boundary layer is the limiting step in the transport mechanism, increasing the turbulence will reduce the boundary layer thickness and so the phenol flux will increase. In previous runs the magnetic stirrer was operating at full speed (approx. 1000 rpm). In this part of the investigation runs were carried out either without stirring, or using a stirring rate of approximately 500 rpm.

Phenol conc. (ppm)	No stirring ($g/hour/m^{-2}$)	500 RPM approx. ½ speed ($g/hour/m^{-2}$)	1000 RPM approx. full speed ($g/hour/m^{-2}$)
1,000	7 ± 3	8± 3	8± 3
2,500	17± 3	20± 3	19± 3
5,000	23± 3	40± 3	38± 3
10,000	43± 5	70± 5	72± 5
15,000	57± 5	98± 5	95± 5

Table 4.13 Phenol fluxes at different stirring rates.

As is apparent from the results in table 4.13, the fluxes for the non-stirred runs are generally considerable lower than for the two stirred runs. As the fluxes for the two types of stirred run are the same within experimental error, transport through the boundary layer is not the rate determining step when the solution is stirred at a rate of 500 rpm or over.

4.2.1.6 EFFECT OF NaOH CONCENTRATION ON PHENOL FLUX

Batch runs showed that the NaOH concentration in the stripping phase plays an important role in the amount of phenol extracted and that a threshold concentration of NaOH exists, above which all the phenol is in the form of the phenate ion in the stripping phase. The percentage extraction of phenol is dependant on NaOH

concentration until this threshold NaOH concentration is reached, but beyond it the percentage phenol extracted is independent of NaOH concentration for a given system.

The runs in which the stripping phase consists of 0.1M NaOH should contain sufficient base to convert the phenol in the stripping phase almost entirely into the phenate ion. Changing to a stripping phase of 0.2M NaOH did not effect the fluxes (see table 4.14), so confirming that a NaOH concentration of 0.1M is not a limiting factor in these experiments. Consequently all other runs were carried out using 0.1M NaOH as the stripping phase.

Phenol conc. (ppm)	Fluxes with 0.1M NaOH as the stripping phase ($g/hour/m^{-2}$)	Fluxes with 0.2M NaOH as the stripping phase ($g/hour/m^{-2}$)
10,000	70 ± 5	70 ± 5
15,000	98 ± 5	99 ± 5
20,000	122 ± 5	121 ± 5
25,000	140 ± 5	143 ± 5

Table 4.14 Phenol fluxes using different NaOH concentration in the stripping phase.

4.2.1.7 EFFECT OF FEED pH ON PHENOL FLUX

To determine whether the magnitude of the pH gradient across the membrane has any effect on phenol fluxes, investigations were carried out using a feed phase solution consisting of 0.1M HCl and phenol (pH 1). The results were compared with analogous runs using aqueous phenol solutions (pH 5) as the feed phase (see table 4.15).

Initial feed phase phenol conc. (ppm)	Flux with aqueous phenol feed phase (g/hour/m^{-2})	Flux with a 0.1M HCl/phenol feed phase (g/hour/m^{-2})
10,000	72 ± 5	72 ± 5
15,000	98 ± 5	99 ± 5
20,000	122 ± 5	120 ± 5
25,000	140 ± 5	139 ± 5

Table 4.15 Phenol fluxes with different feed phases.

We can conclude that the flux is not affected by the addition of HCl to the feed phase, and that the magnitude of the pH gradient does not affect the flux within the pH ranges used in these investigations. As the phenol in the feed phase is in both cases over 99.9% in the unionised form, the phenol concentration gradient across the membrane is essentially the same.

4.2.2 EFFECT OF AMINE CONCENTRATION ON PHENOL FLUXES

In conventional SLMs increasing the carrier concentration increases the flux. The same relationship should apply for the integrated SLMs used in this investigation. Three different amine functionalised poly(organosiloxane)s were used in this part of the investigation. These contained 4 mole % amine loading A1, 11 mole % amine loading A2 and 30 mole % amine loading A3 (see section 2.2.3).The phenol fluxes for each of these polymers with various feed concentration are shown in table 4.16.

Initial feed phase phenol conc. (ppm)	PDMS (g/hour/m^{-2})	A1 (4% amine) (g/hour/m^{-2})	A2 (11% amine) (g/hour/m^{-2})	A3 (30% amine) (g/hour/m^{-2})
1,000	3± 3	7 ± 3	8 ± 3	11 ± 3
2,500	7 ± 3	12 ± 3	21 ± 3	40 ± 3
5,000	12 ± 3	25± 3	38 ± 3	75 ± 3
10,000	31 ± 5	45 ± 5	70 ± 5	113 ± 5
15,000	35± 5	56 ± 5	92 ± 5	150 ± 5
20,000	43 ± 5	65 ± 5	122 ± 5	175 ± 5
25,000	55 ± 5	76 ± 5	140 ± 5	190 ± 5
30,000	60 ± 5	85 ± 5	162 ± 5	211 ± 5
35,000	68 ± 5	98 ± 5	181 ± 5	234 ± 5

Table 4.16 Phenol fluxes for the amine poly(organosiloxane)s.

The results show that the phenol fluxes increase with increase in the amine loading. Phenol fluxes obtained for transport through A3 are *ca* 3.5 times greater than those found using PDMS and similarly A2 *ca* 2.5 times and A1 *ca* 1.5 times that through PDMS (see figure 4.3).

The results from the batch experiments indicated that increasing the amine concentration in the amine functionalised poly(organosiloxane) increases the phenol solubility in the polymer, and that this results in increased fluxes (see equation 1.1). The results shown in table 4.16 do not differentiate between facilitated transport and an increase in the solubility of phenol in amine-containing polymers.

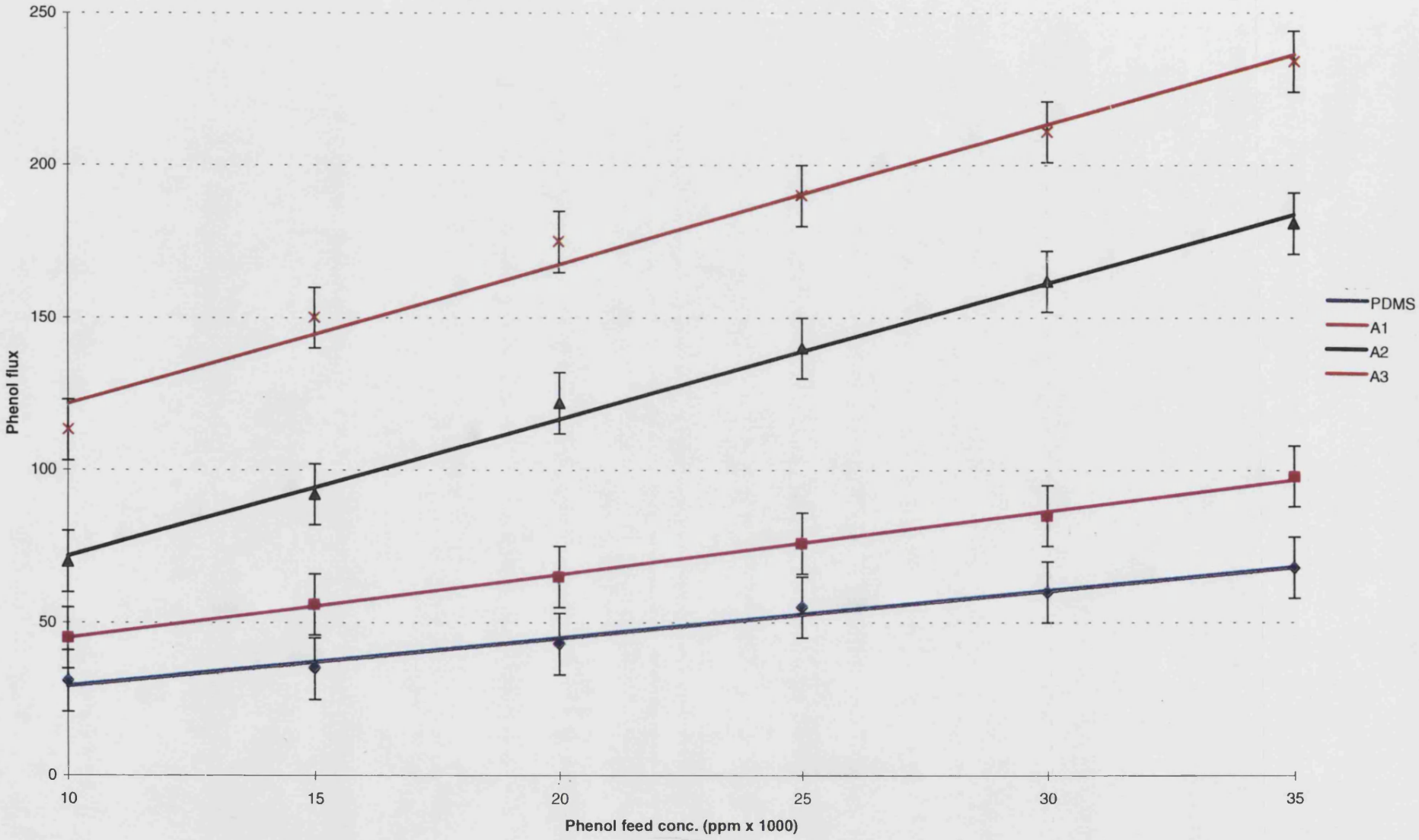


Figure 4.3 Phenol fluxes through A1-A3 and PDMS.

4.2.3 THE EFFECT OF A ZERO pH GRADIENT ACROSS THE MEMBRANE ON PHENOL FLUX

Experiments were carried out in which there was no pH gradient across the membrane. For the amine to act as a carrier a pH gradient must be applied with the basic stripping phase causing the phenol/amine complex to de-complex and generate phenate anion. Thus comparing fluxes with and without a pH gradient will give a indication of the degree of facilitated transport occurring for a specific functionalised membrane.

In these experiments distilled water was used as the stripping phase. The slight pH gradient at the start of each run is reduced to effectively zero as soon as phenol enters the stripping phase. The results from the transported studies using A2 (11% amine) membrane are shown in table 4.17.

Initial feed phase phenol conc. (ppm)	Fluxes with as 0.1M NaOH as the stripping phase (g/hour/m^{-2})	Fluxes with distilled water as the stripping phase (g/hour/m^{-2})
10,000	70 ± 5	53 ± 5
15,000	95 ± 5	68 ± 5
20,000	122 ± 5	87 ± 5
25,000	140 ± 5	98 ± 5
30,000	160 ± 5	110 ± 5
35,000	181 ± 5	143 ± 5

Table 4.17 Phenol fluxes using water and 0.1M NaOH as stripping phases.

The phenol fluxes in experiments in which distilled water was used as the stripping phase are higher than the phenol fluxes using PDMS SLMs. This is due to the increase in solubility of phenol in the amine functionalised poly(organosiloxane). The phenol fluxes are significantly lower in experiments in which distilled water is used as the stripping phase. Thus it is likely that the amine is involved in a facilitated transport mechanism.

To calculated the flux due to facilitated transport, the effect of the increase in phenol solubility must be taken into account. This cannot be achieved by simply subtracting the phenol fluxes from water only runs from fluxes in which NaOH was used as the stripping phase, as the two system have different unionised phenol concentrations gradients across the membrane at steady state.

The steady state unionised phenol concentration gradient is the same as the feed phase phenol concentration in runs in which a NaOH stripping phase was used. Phenol is completely ionised in a 0.1M NaOH stripping phase but is completely unionised within the feed phase. With a distilled water stripping phase the unionised phenol concentration gradient is the difference between feed phase phenol concentration and the steady state phenol concentration within the stripping phase, as phenol is in the unionised form on both sides of the membrane.

The phenol fluxes obtained using distilled water as the stripping phase have been corrected in table 4.18 to show the fluxes as if they had the same concentration gradients as the analogous NaOH stripping phase runs. Data for each initial phenol feed phase concentration was corrected by using equation below;.

$$J_{cor} = (\Delta C_{NaOH} / \Delta C_{water}) \times J_{water}$$

ΔC_{NaOH} = Initial phenol feed phase concentration.

ΔC_{water}= Initial phenol feed phase concentration subtracted by the steady state phenol concentration in the distilled water stripping phase.

J_{water} = Phenol flux when distilled water is used as the stripping phase.

J_{cor} = Corrected phenol flux for the distilled water stripping phase run.

Corrected phenol fluxes for runs using water stripping phases have been subtracted from the phenol fluxes from the analogous NaOH stripping phase runs, to

give the facilitated fluxes. These results are summarised in table 4.18 for each amine functionalised poly(organosiloxane).

Polymer	Feed phase phenol conc. (ppm)	Unionised phenol conc. gradients with NaOH stripping phase (ppm) ΔC_{NaOH}	Unionised phenol conc. gradients with water stripping phase (ppm) ΔC_{water}	ΔC_{NaOH} /ΔC_{water}	Phenol flux (water stripping phase) g/hour/m^{-2}	Corrected phenol flux (water stripping phase) g/hour/m^{-2}	Phenol flux (0.1M NaOH stripping phase) g/hour/m^{-2}	Facilitated flux g/hour/m^{-2}
A1	10,000	10,000	9,250	1.081	28 ± 5	31 ± 5	45 ± 5	14 ± 10
A1	15,000	15,000	14,100	1.064	34 ± 5	36 ± 5	55 ± 5	19 ± 10
A1	20,000	20,000	18,800	1.064	45 ± 5	48 ± 5	65 ± 5	17 ± 10
A1	25,000	25,000	20,200	1.064	56 ± 5	60 ± 5	76 ± 5	16 ± 10
A1	30,000	30,000	28,400	1.064	68 ± 6	72 ± 5	85 ± 5	13 ± 10
A1	35,000	35,000	32,800	1.067	83 ± 5	88 ± 5	98± 5	10 ± 10
A2	10,000	10,000	8,600	1.160	53 ± 5	62 ± 5	70 ± 5	0 to 18
A2	15,000	15,000	13,200	1.140	68 ± 5	78 ± 5	95 ± 5	17 ± 10
A2	20,000	20,000	17,650	1.133	87 ± 5	99 ± 5	122 ± 5	25 ± 10
A2	25,000	25,000	22,400	1.116	98 ± 5	109± 5	146 ± 5	31 ± 10
A2	30,000	30,000	27,150	1.107	110 ± 5	122 ± 5	160 ± 5	38 ± 10
A2	35,000	35,000	31,500	1.111	132 ± 5	147 ± 5	181 ± 5	34 ± 10
A3	10,000	10,000	8,300	1.025	64± 5	77 ± 5	113 ± 5	36 ± 10
A3	15,000	15,000	12,550	1.195	92± 5	110 ± 5	150 ± 5	40 ± 10
A3	20,000	20,000	17,400	1.149	98 ± 5	113 ± 5	172 ± 5	62 ± 10
A3	25,000	25,000	22,000	1.136	113 ± 5	129 ± 5	190 ± 5	61 ±10
A3	30,.000	30,000	26,500	1.132	132 ± 5	149 ± 5	211 ± 5	62 ± 10
A3	35,000	35,000	30,800	1.136	158 ± 5	180 ± 5	234 ± 5	54 ± 10

Table 4.18 Facilitated fluxes at various phenol feed concentrations for each of the amine functionalised poly(organosiloxane)s.

All the amine functionalised poly(organosiloxane)s show a facilitation effect, with facilitated fluxes increasing with increase in amine loading. These effects are analogous to those exhibited by conventional amine carriers[87-90] in that the facilitated flux is directly related to carrier concentration, and it also increases with increasing feed concentration until the saturation point is reached. At this point flux becomes independent of feed substrate concentration.

Figure 4.4 shows these features very clearly. Facilitated fluxes through membrane A1 are independent of feed phenol concentration over the range studied. Thus saturation point has been reached using a feed phenol concentration of 10,000 ppm. A2 reaches saturation point with a feed phenol concentration of *ca* 15,000-20,000 ppm and a facilitated flux of *ca* 35 g/hour/m^{-2} (compared with around 15 g/hour/m^{-2} for A1). Membrane A3 is also saturated by a phenol feed concentration of *ca* 20,000 ppm phenol but the facilitated flux is higher at *ca* 60 g/hour/m^{-2}.

These results are as expected for a facilitated transport process in which the amine functional group is acting as a carrier for unionised phenol. However, it is difficult to compare the results of this study in detail with results in the literature for phenol transport using other amine carrier SLMs as each study has been performed under very different conditions and the results are reported in different ways. The most relevant study is that of Liu[88] in which TOA/sulphuric acid is used as a carrier dissolved in octanol as the liquid membrane. The feed phenol concentration was 5,000 ppm and the phenol flux for this system was 6 g/hour/m^{-2}. The overall phenol flux through A2 at 5,000 ppm of phenol is 40 g/hour/m^{-2}, i.e. more than 6 times the phenol flux reported by Liu[88].

Although the facilitated phenol flux is not know for the amine functionalised poly(organosiloxane)s using a feed concentration of 5,000 ppm, both A1 and A2 have facilitated fluxes of *ca* 10 g/hour/m^{-2} at a 10,000 ppm phenol feed concentration. These values are approximately the same as those reported by Liu[88]. A3 (30% amine loading) has a facilitated flux of 36 g/hour/m^{-2} at 10,000 ppm which is 6 times the flux reported

by Liu[88]. This difference cannot be explained by the difference in feed phenol concentration. It is possible that the greatly increased facilitated flux of phenol through membrane A3 results from a change in transport mechanism. At high amine loadings a "jumping" mechanism may also transport the phenol across the membrane. A mechanism in which phenol "jumps" from one amine site on the polymer to another is likely to be faster than just an amine/phenol complex diffusion mechanism as seems likely to occur for A1 and A2. It could be confirmed that a "jumping" mechanism is dominant by altering the membrane thickness and determining the effect on flux. If the same mechanism is in operation in all cases the relative effect on the fluxes will be the same, but if A3 involves a "jumping" mechanism than the effect of altering the membrane thickness will be different to that of A1 and A2. This investigation was not carried out due to the difficulty of obtaining celguard supports of varying thickness.

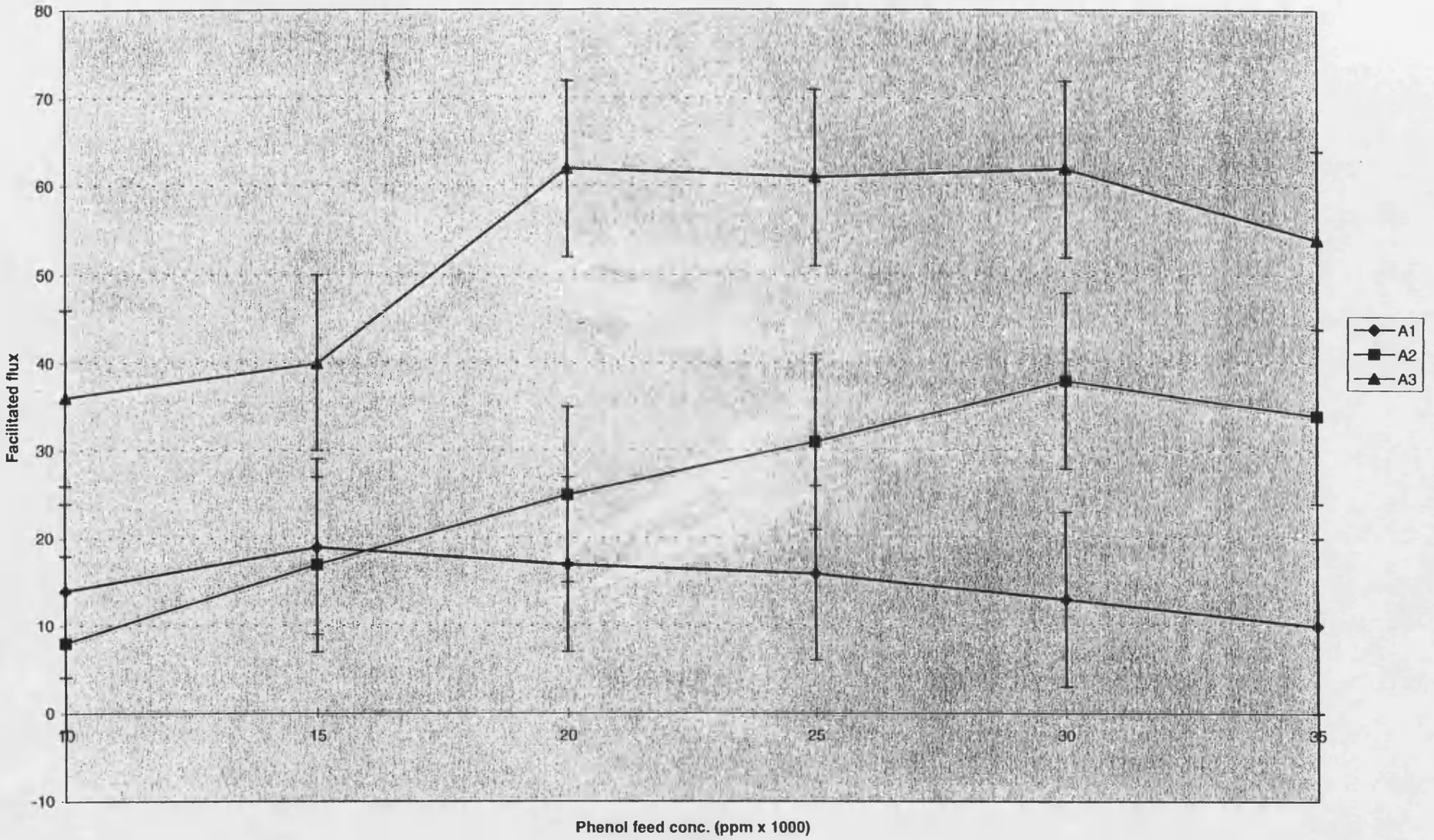


Figure 4.4 Facilitated phenol flux through A1-A3.

4.3 TRANSPORT OF PHENOL DERIVATIVES USING AMINE FUNCTIONALISED POLY(ORGANOSILOXANE) SLMs

4.3.1 TRANSPORT OF HYDROQUINONE

The aim in the sets of experiments described in section 4.3 was to determine the effect of changing the pK_a of the substrate without changing its structural type, on facilitated fluxes and on the transport mechanism. This was achieved by using ring substituted phenols. In the continuous flow experiments in this section two types of stripping phases were used, 0.1M NaOH and distilled water unless stated otherwise. All the batch runs were carried out with 1.0M NaOH as the stripping phase. Hydroquinone (Hy) has a second hydroxyl group in the para position of the ring which changes the pK_a from 9.89 in phenol to 10.35 in hydroquinone. This can be attributed to the resonance contributions shown in figure 4.5.

Figure 4.5 Hydroquinone resonance forms

Hydroquinone conc. (ppm)	Fluxes with 0.1M NaOH stripping phase ($g/hour/m^{-2}$)
10,000	8 ± 5
15,000	9 ± 5
20,000	8 ± 5
25,000	8 ± 5
30,000	8 ± 5
35,000	8 ± 5

Table 4.19 Hydroquinone fluxes through A1.

As hydroquinone fluxes through A1 were very low when using 0.1M NaOH as the stripping phase, experiments employing a water stripping phase were not carried out for A1. The very low permeability of hydroquinone compared to that of phenol is probable due to the lower solubility of hydroquinone in PDMS. Facilitated fluxes for hydroquinone were calculated by the same procedure used for phenol, and the results are summarised in table 4.20.

Polymer	Feed phase Hy conc. (ppm)	Unionised Hy conc. gradients with NaOH stripping phase (ppm) ΔC_{NaOH}	Unionised Hy conc. gradients with water stripping phase (ppm) ΔC_{water}	$\Delta C_{NaOH} / \Delta C_{water}$	Hy flux (water stripping phase) g/hour/m^{-2}	Corrected Hy flux (water stripping phase) g/hour/m^{-2}	Hy flux (0.1M NaOH stripping phase) g/hour/m^{-2}	Facilitated flux g/hour/m^{-2}
A2	10,000	10,000	9,850	1.015	7 ± 5	7 ± 5	25 ± 5	18 ± 10
A2	15,000	15,000	14,850	1.010	7 ± 5	7 ± 5	33 ± 5	26 ± 10
A2	20,000	20,000	19,800	1.010	10 ± 5	10 ± 5	33 ± 5	23 ± 10
A2	25,000	25,000	24,750	1.010	15 ± 5	15 ± 5	37 ± 5	22 ± 10
A2	30,000	30,000	29,750	1.008	15 ± 5	15 ± 5	44 ± 5	29 ± 10
A2	35,000	35,000	34,700	1.009	15 ± 5	16 ± 5	48 ± 5	32 ± 10
A3	15,000	15,000	14,900	1.049	34 ± 5	35 ± 5	74 ± 5	39 ± 10
A3	20,000	20,000	19,300	1.036	34 ± 5	35 ± 5	83 ± 5	48 ± 10
A3	25,000	25,000	23,900	1.046	42 ± 5	43 ± 5	88 ± 5	45 ± 10
A3	30,000	30,000	28,800	1.042	48 ± 5	50 ± 5	108 ± 5	58 ± 10
A3	35,000	35,000	33,500	1.045	57 ± 5	60 ± 5	105 ± 5	45 ± 10

Table 4.20 Hydroquinone (Hy) fluxes through A2 and A3.

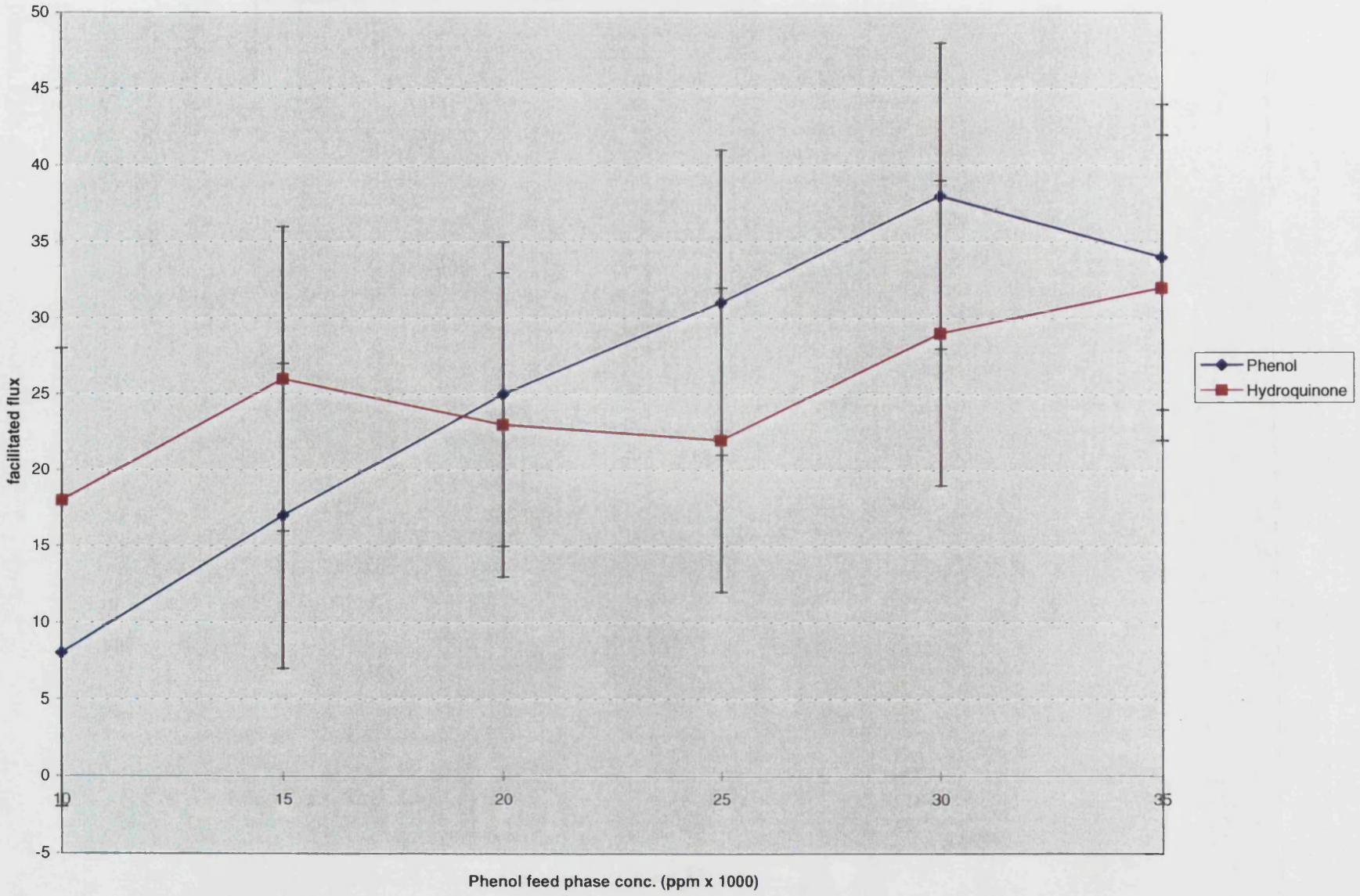


Figure 4.6 Hydroquinone and phenol facilitated fluxes through A2.

Figure 4.6 provides a comparison between hydroquinone and phenol facilitated fluxes. These are approximately the same for both substrates although the overall fluxes are very different. It seem likely therefore that the same transport mechanism is operating in both systems.

4.3.2 TRANSPORT OF p-METHOXYPHENOL

p-Methoxyphenol has a pK_a of 10.17. The higher pK_a results from the electron donating ability of the methoxy groups. The same types of transport experiments were carried out using this substrate, but only at a feed concentration of 15,000 ppm, which corresponds to the maximum solubility of methoxyphenol in water.

Polymer	Feed phase methoxy phenol conc. (ppm)	Unionised methoxy phenol conc. gradients with NaOH stripping phase (ppm) ΔC_{NaOH}	Unionised methoxy phenol conc. gradients with water stripping phase (ppm) ΔC_{water}	ΔC_{NaOH} /ΔC_{water}	Methoxy phenol flux (water stripping phase) g/hour/m^{-2}	Corrected methoxy-phenol flux (water stripping phase) g/hour/m^{-2}	Methoxy-phenol flux (0.1M NaOH stripping phase) g/hour/m^{-2}	Facilitated flux g/hour/m^{-2}
A1	15,000	15,000	14,270	1.051	23 ± 5	24 ± 5	31 ± 5	0 to 17
A2	15,000	15,000	13,800	1.087	45 ± 5	49 ± 5	68 ± 5	19 ± 10
A3	15,000	15,000	13,000	1.154	76 ± 5	87 ± 5	107 ± 5	20 ± 10

Table 4.21 Methoxyphenol fluxes through each of three amine functionalised poly(organosiloxane)s.

The methoxyphenol facilitated fluxes for A1 and A2 are of the same order as those for phenol, whereas the flux through A3 for the former is about half that of phenol. Flux differences through A3 could reflect a change in the transport mechanism with methoxyphenol unable to participate in a "jumping" mechanism (see section 4.2.3).

The weaker acidic nature of methoxyphenol compared to phenol may be responsible for this difference in behaviour.

4.3.3 TRANSPORT OF p-BROMOPHENOL

p-Bromophenol has a pK_a of 9.18, which is significantly lower than that of phenol and results from the electron withdrawing nature of the bromo group. Transport experiments were carried out as for phenol but only at a bromophenol feed concentration of 15,000 ppm, due to the limited solubility of bromophenol in water.

Polymer	Feed phase bromophenol conc. (ppm)	Bromophenol flux (water stripping phase) g/hour/m^{-2}	Bromophenol flux (0.1M NaOH stripping phase) g/hour/m^{-2}
A1	15,000	217 ± 5	260 ± 5
A2	15,000	226 ± 5	264 ± 5

Table 4.22 Fluxes for the transport of bromophenol through membranes A1 and A2.

No results could be obtained for the A3 SLM as it was not stable over a 4 hour period in the presence of bromophenol. The bromophenol fluxes for A1 and A2 are very large in comparison to the analogous phenol fluxes, with extractions of bromophenol being *ca* 6,000 ppm when using water as the stripping phase, and *ca* 7,000 ppm when using 0.1M NaOH as the stripping phase. No facilitated flux was calculated for these systems, as the concentration gradient of unionised bromophenol across the membrane when using a 0.1M NaOH stripping phase is not known as a function of time. In the course of the experiments the pH of the stripping phase fell to *ca* pH 11.8, at which value a significant quantity of unionised bromophenol will be present in the stripping phase (*ca* 20%) see equation 4.2. The overall bromophenol fluxes are higher than analogous overall phenol fluxes by a factor of almost 3 for A2. Solubility differences in PDMS for bromophenol compared with phenol account for the higher extraction figure for the former (see table 4.23).

4.3.4 BATCH RUNS ON PHENOL DERIVATIVES

Batch studies were carried out to determine whether the percentage extraction of several phenol derivatives were similar, as structurally these compounds are closely related. In all cases the feed phase had an initial substrate concentration of 15,000 ppm and the striping phase was 1.0M NaOH.

Compound	PDMS (%)	A1 (4% amine) (%)	A2 (11% amine) (%)	A3 (30% amine) (%)
Phenol	65 ± 2	80 ± 2	92 ± 2	93 ± 2
Hydroquinone	<40	<40	<40	<40
Methoxyphenol	47 ± 2	67 ± 2	92 ± 2	92 ± 2
Bromophenol	80 ± 2	90 ± 2	Failed	Failed

Table 4.23 Batch runs for phenol and phenol derivatives at a feed concentration of 15,000 ppm.

The A1 SLM is the only one of the three SLMs to be stable for each of the substrates for the whole duration of the experiments. The percentage extraction through this single SLM follows the order bromophenol > phenol > methoxyphenol .> hydroquinone. This is the same sequence as the overall fluxes achieved in the continuous run experiments. The overall substrate fluxes are determined to a large degree by the solubility of the unionised form of the substrate in PDMS, and these results indicate that the percentage extraction of a given substrate in a batch experiment is controlled by the same factor.

4.4 THE TRANSPORT OF BENZYL ALCOHOL AND PHENOXYACETIC ACID

4.4.1 THE TRANSPORT OF BENZYL ALCOHOL USING AMINE FUNCTIONALISED POLY(ORGANOSILOXANE) SLMs

The aim of these transport experiments was to determine the way an extremely weakly acidic compound is transported through an amine functionalised poly(organosiloxane) SLM. Benzyl alcohol was chosen as the model substrate as it is an aromatic alcohol of similar steric size and shape to that of phenol (figure 4.7).

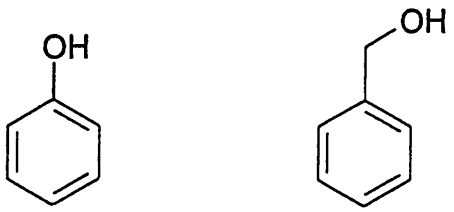


Figure 4.7 Phenol and benzyl alcohol

Two sets of experiments were carried out. In the first a pH gradient was applied across the membrane by using 0.1M NaOH as the stripping phase. In the second set of experiments distilled water was used as the stripping phase so that a concentration gradient was the major driving force. The benzyl alcohol feed concentrations ranged from 10,000 to 35,000 ppm. The results from these transport experiments are summarised in table 4.24.

Polymer	Feed phase benzyl alcohol conc. (ppm)	Fluxes g/hour/m^{-2} (Water stripping phase) A	Fluxes g/hour/m^{-2} (NaOH stripping phase) B	Difference (A-B) (g/hour/m^{-2})
A1	10,000	17 ± 5	17 ± 5	0 ± 10
A1	15,000	37 ± 5	30 ± 5	7 ± 10
A1	20,000	49 ± 5	44 ± 5	5 ± 10
A1	25,000	62 ± 5	61 ± 5	1 ± 10
A1	30,000	80 ± 5	74 ± 5	6 ± 10
A1	35,000	93 ± 5	91 ± 5	2 ± 10
A2	10,000	49 ± 5	44 ± 5	5 ± 10
A2	15,000	74 ± 5	64 ± 5	10 ± 10
A2	20,000	92 ± 5	86 ± 5	6 ± 10
A2	25,000	110 ± 5	110 ± 5	0 ± 10
A2	30,000	128 ± 5	137 ± 5	9 ± 10
A2	35,000	157 ± 5	150 ± 5	7 ± 10
A3	10,000	74 ± 5	81 ± 5	-7 ± 10
A3	15,000	127 ± 5	127 ± 5	0 ± 10
A3	20,000	167 ± 5	158 ± 5	9 ± 10
A3	25,000	211 ± 5	210 ± 5	1 ± 10
A3	30,000	255 ± 5	246 ± 5	9 ± 10
A3	35,000	299 ± 5	294 ± 5	5 ± 10

Table 4.24 Benzyl alcohol fluxes through amine functionalised poly(organosiloxane)s.

These results show that no facilitated transport occurs for benzyl alcohol with any of the amine functionalised poly(organosiloxane)s SLMs. The O-H group in benzyl alcohol is not sufficiently acidic to interact strongly with the amine functional group in A1, A2 or A3, and it appears that dipole-dipole interactions are insufficient to provide

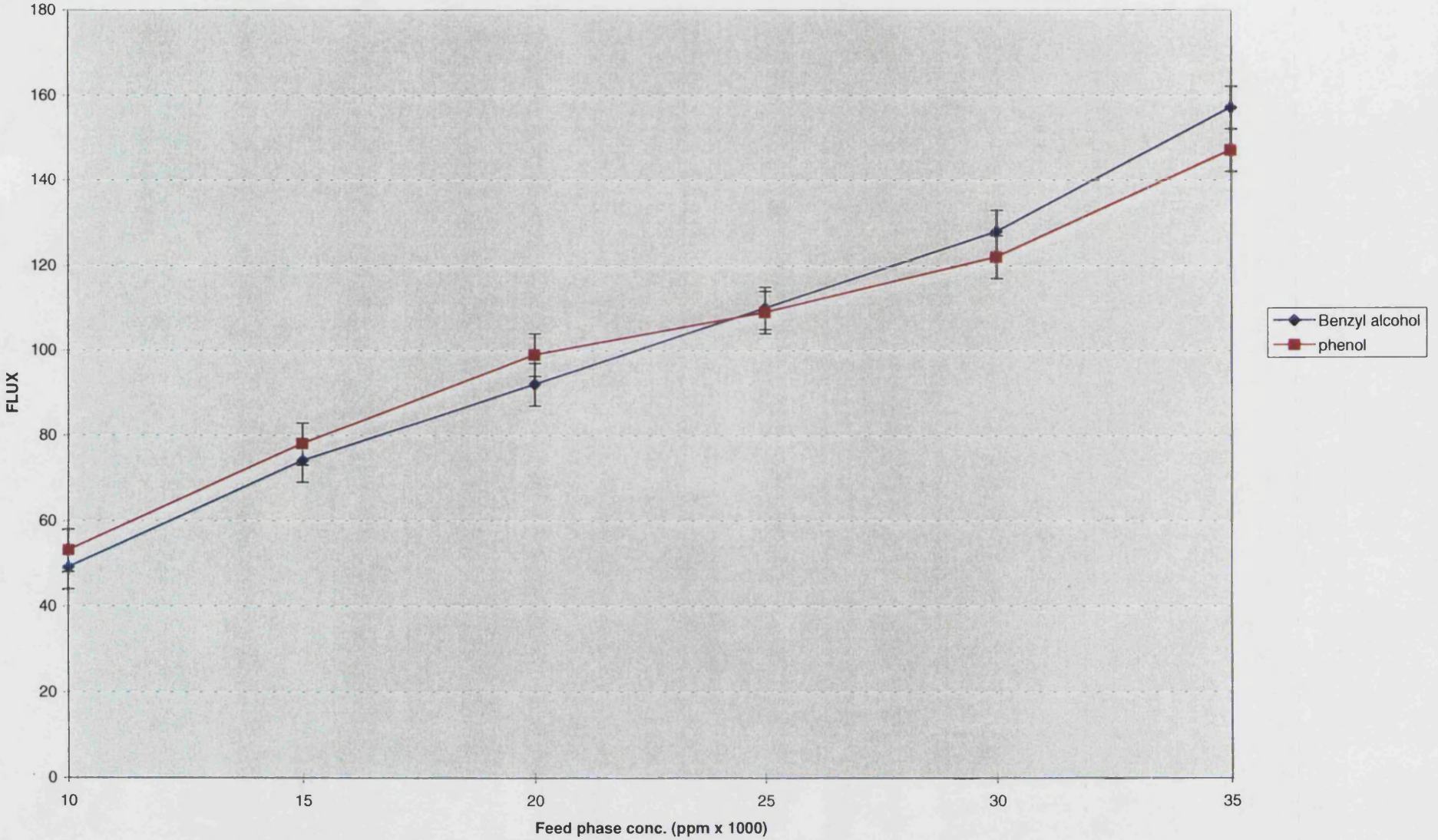


Figure 4.8 Phenol and benzyl alcohol fluxes through A2 with a water stripping phase.

facilitated transportation. We note that the fluxes for benzyl alcohol are comparable to the fluxes for phenol when water is used as the stripping phase (Figure 4.8).

4.4.2 TRANSPORT OF PHENOXYACETIC ACID THROUGH AMINE FUNCTIONALISED POLY(ORGANOSILOXANE) SLMs

The aim of these transport experiments was to determine whether the facilitated flux of phenoxyacetic acid is higher than that of phenol through a siloxane SLM containing a basic functional group. Phenoxyacetic acid was chosen as it is water soluble to the extent of 10,000 ppm and it can be determined quantitatively by UV sepectrophotometry. It also has a pK_a of 5.12 which is considerable lower than that of phenol at 9.89. If the amine forms a stronger complex with phenoxyacetic acid than with phenol it can have one of two effects on the facilitated flux. It can increase the flux compared with that observed for phenol as the complex is less likely to de-complex within the membrane. It can also have the opposite effect. If the complex formed is too strong it can prevent decomplexation on the membrane/stripping phase interface in the absence of sufficiently strong base. The transport experiments were first carried out using 0.1M NaOH as the stripping phase, as this would ensure that decomplexation occurred.

Polymer	A1	A2	A3
Flux (g/hour/m^{-2})	4 ± 5	6 ± 5	10 ± 5

Table 4.25 Phenoxyacetic acid fluxes.

Table 4.25 shows the fluxes to be very low under these conditions. It appears likely that phenoxyacetic acid has a very low solubility in amine functionalised poly(organosiloxane)s and that solubility is a major factor in determining the magnitude of the flux. As a consequence of this observation, no further studies were carried out.

4.5 STABILITY OF AMINE FUNCTIONALISED POLY(ORGANOSILOXANE) SLMs

The generally low working lifetime of SLMs is one very important reason why SLM technology has not been used more frequently in industry. One of the aims of this project was to determine whether replacement of conventional carrier/solvent systems by poly(organosiloxane)s leads to a improvement in this property. The working lifetimes of A1-A3 SLMs as a function of aqueous phenol in the stripping phase are shown in figure 4.9. This reveals that the A3 SLM failed after *ca* 24 hours of operation, but that A1 and A2 were still working at optimum rate after 50 hours. Leaching causes SLM failure and this could be easily observed as the celguard support becomes completely opaque when the polymer has been completely leached from it. In the case of A1 some one-third of the celguard support was opaque after 3 days operation. Increasing the amine content of the PDMS reduced the stability of this type of SLM.

During the batch and continuous run experiments for the various phenol derivatives (see section 4.3) it became clear that a link exits between SLM stability and the flux of the substrate being transported. Large fluxes decrease the stability of the SLM. The most likely explanation for this greater instability is the increase in osmotic pressure across the membrane as flux increases. Studies carried out by Dozol[72] *et al* confirm increasing osmotic pressure across a membrane can lead to greater instability of a SLM.

The working lifetimes of amine functionalised poly(organosiloxane) SLMs are comparable with those of amine carrier[87-90] and solvent[80] systems involving flat sheet supports. An amine carrier[87] has been reported to be stable for 80 days using hollow fibre modules and, it would be interesting to determine in future work whether fluid poly(organosiloxane) SLMs have an increased lifetime in hollow fibre modules.

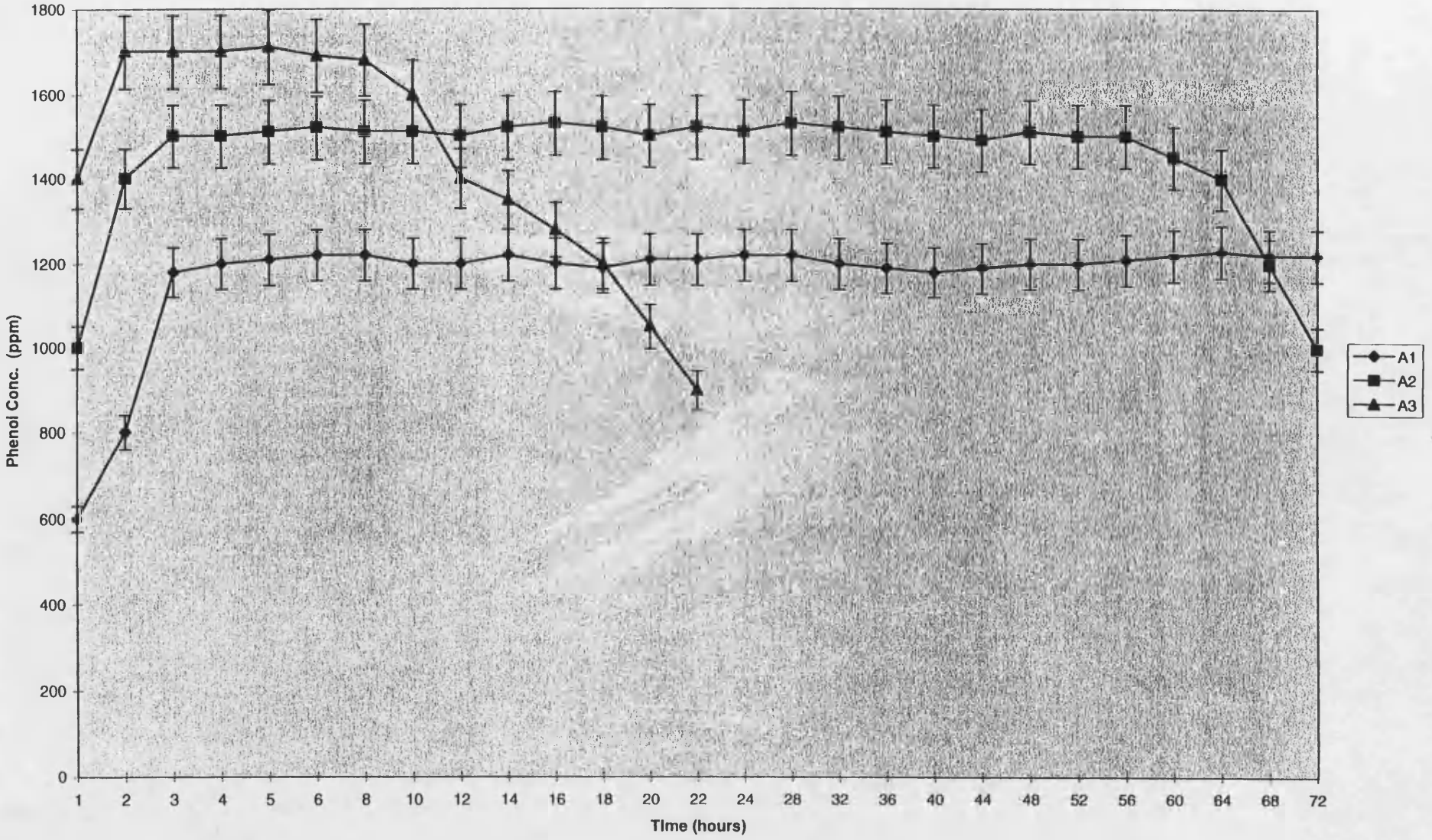


Figure 4.9 Working lifetimes of A1-A3 SLMs.

4.6 SPECTROPHOTOMETIC AND ^{1}H NMR INVESTIGATIONS OF THE H-BONDING BETWEEN PHENOL AND AMINE FUNCTIONALISED POLY(ORGANOSILXANE)S

The nature and strength of H-bonding interactions between amines and alcohols (alkyl and aryl) have been investigated by a variety of techniques. One of the most useful for the solid-state is X-ray crystallography, and the complexes[130,131] formed between primary amines and alcohols have been studied in the greatest detail. The crystal structure studies of solid primary amines have shown that their valencies for hydrogen bonding are not completely satisfied. The amine group has two donor H atoms but only one acceptor lone pair. Therefore, crystalline primary amines typically form only one hydrogen bond per amine group[130] (see figure 4.10). The solid-state structures of alkyl alcohols[130] also show that their H-bonding valencies are not completely satisfied. In this case because ROH possesses two lone pairs but only one H-atom capable of H-bonding. Co-crystals of primary amines and alkyl alcohols usually form hydrogen-bonded complexes in which all the lone pairs and all electropositive H atoms on N and O are involved. These structures typically reveal three bonds to hydrogen around each O and N atom, so these complexes are referred to as saturated hydrogen bonding (SHB) complexes. The major driving force for the formation of these SHB complexes is the 50% increase of the number of hydrogen bonds as compared with the uncomplexed constituents.

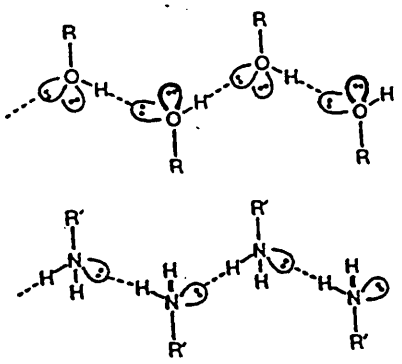


Figure 4.10 Usual chain-like H-bonding pattern for primary amines and alkyl alcohols.

X-ray crystallographic investigations[130,131] of phenol and primary amine complexes have shown that they do not form SHB complexes. The primary amine donates, and phenol accepts a single H atom (figure 4.11). Stacking of the aromatic rings of the phenol in the crystal constrains the amount of H-bonding possible.

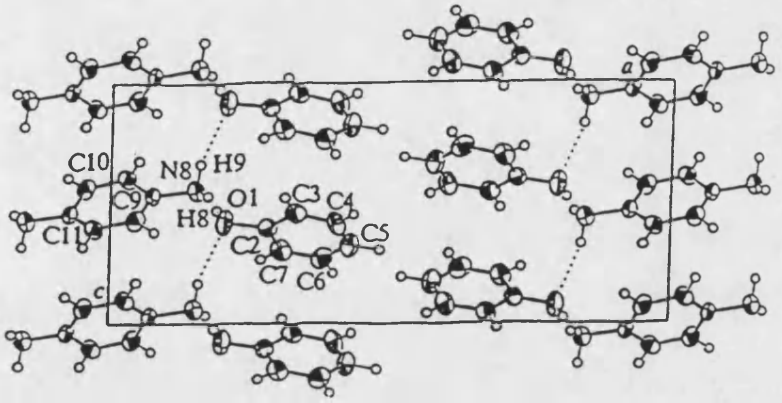


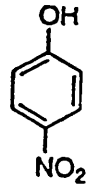
Figure 4.11 p-Phenylenediamine-phenol complex.

Other techniques used to investigate the interactions between amines and phenol include IR[132-136] spectroscopy. The O-H_{vib} maxima of phenol and phenol/amine complexes formed in the gas phase are reported in table 4.26. Hydrogen-bonding through the O-H of phenol to an amine group causes the O-H_{vib} maxima to appear at lower frequencies in the IR spectrum. The data in table 4.26 show that as the amine becomes more basic, the O-H_{vib} maxima shift to lower frequency, indicating an increase in the strength of the H-bonding.

Complex	Phenol O-H maxima (cm^{-1})	Shift in phenol O-H maxima (cm^{-1})	pK_a of amine in the complex
Phenol only	3657		
Phenol/NH_3	3294	-363	9.5
Phenol/$N(CH_3)_3$	3067	-590	9.8
Phenol/$N(C_2H_5)_3$	2985	-672	11.0

4.26 The O-H_{vib} maxima for a range of amine/phenol complexes in gas phase.

An uv-vis study was carried out by Mizutani[137] *et al* to determine the binding constants for a range of amines and phenol derivatives (see table 4.27) in toluene. Absorbance changes in the phenol $\pi \rightarrow \pi^*$ band as a function of amine concentration were determined and the data analysed assuming 1:1 complex formation.



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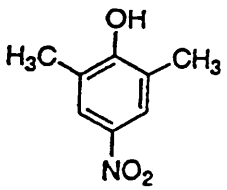

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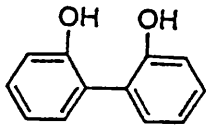

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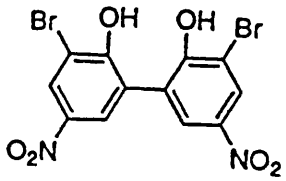

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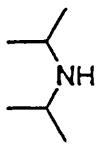

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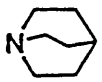

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Host	Guest	K_1 (M^{-1})
1	5	200
1	6	3000
2	5	11
2	6	230
3	5	280
3	6	4600
4	5	$>10^6$
4	6	$>10^6$

Table 4.27 Binding constants (K_1) of phenol-amine complexes at 25^0C in toluene.

The range of binding constants is large showing the dramatic effect of addition of electron donating or withdrawing substituents on phenol. However binding constants are only one factor in facilitated transport mechanism. As noted in section 1.3 the binding constants of TPP/Mn^{3+} to CN^- and aza-18-crown-6 to Cd^{2+} are $7x10^2$ and $5x10^5$ M^{-1} respectively but both systems are very effective in SLMs.

4.6.1 IR STUDIES OF THE INTERACTIONS BETWEEN PHENOL AND AMINE FUNCTIONALISED POLY(ORGANOSILOXANE)S

A limited IR investigation of the H-bonding between phenol and the NMe_2 groups in amine functionalised poly(organosiloxane)s was carried out as part of this project. Solid phenol was dissolved in the amine functionalised poly(organosiloxane)s A1-A3 (*ca* 20% phenol wt/wt), and the IR spectrum of the resulting fluid recorded between NaCl plates.

A1 (cm^{-1})	A2 (cm^{-1})	A3(cm^{-1})	PDMS (cm^{-1})	C3 (30% Butyl) (cm^{-1})
3337 ± 4	3331 ± 4	3330 ± 4	3382 ± 4	3383 ± 4

Table 4.28 O-H_{str} peak maxima of phenol dissolved in a range of poly(organosiloxane)s including PDMS.

The OH_{str} maxima of phenol in the gas phase[132] appears at 3657 (± 2) cm^{-1}, whereas the OH_{str} maxima of phenol in the solid phase appears at 3327 (± 4) cm^{-1}. This reflects significant H-bonding in the solid as confirmed by X-ray crystallography[131,132]. The OH_{str} maxima of phenol dissolved in PDMS was observed at 3382 cm^{-1}. As noted before phenol can hydrogen bond to organic substrates (including itself) in organic solvents, so the OH_{str} maxima of phenol in PDMS at 3382 cm^{-1} has been taken as the "blank" in this study, indicating an unknown amount of intra/inter molecular interactions. A very similar value was also found for phenol dissolved in PDMS modified to contain 30 mole % butyl substituents. This stretching frequency value has

been compared to those for phenol dissolved in the amine functionalised poly(organosiloxane)s A1-A3. In all three the OH_{str} appears at lower frequency. This suggests that the side-arm amine functionality does indeed interact with the dissolved phenol. This interaction is likely to be of importance in the facilitated transport mechanism.

4.6.2 ^{1}H NMR STUDIES OF THE INTERACTION OF PHENOL AND ITS DERIVATIVES WITH AMINE FUNCTIONALISED POLY(ORGANOSILOXANE)S

^{1}H and ^{13}C NMR studies[137,138] have been carried out by others to investigate the degree of proton transfer between amines and organic acids including phenol. The H-bonding between amines and phenol can stabilise the transition state for proton transfer between amines and phenol (see below). This process plays an important role in a number of enzymatic reactions[139]. The results from a ^{13}C NMR study[137] indicate that both primary and secondary amines will more readily stabilise proton transfer than tertiary amines.

$$PhOH + NR_3 \overset{K_1}{\rightleftharpoons} [PhOH\cdots NR_3]_{solv}$$

$$[PhOH\cdots NR_3]_{solv} \overset{K_2}{\rightleftharpoons} [PhO^-\cdots HN^+R_3]_{solv}$$

To further investigate the bonding interactions occurring between phenol and amine functionalised poly(organosiloxane), ^{1}H NMR studies were carried.^{13}C NMR studies were not informative because of the complex nature of the resulting spectra. The ^{1}H NMR spectra of A3 containing 20% phenol, or one of its derivatives, was compared with the ^{1}H NMR spectrum of pure A3. Changes in proton chemical shifts for the amine functionality and its spacer chain an addition of phenol are noted in table 4.29. Positive numbers indicate that the signal has moved downfield (higher ppm). The chemical shift of the hydrogens of the hydroxyl groups of the phenol derivatives could not be determined accurately because of the broadness of the signal.

$O\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}N(CH_3)_2$

D A C B

Hydrogen	Phenol (ppm)	Methoxyphenol (ppm)	Bromophenol (ppm)	Phenoxyacetic acid (ppm)
A	0.12 ± 0.02	0.04 ± 0.02	0.02 ± 0.02	0.02 ± 0.02
B	0.14 ± 0.02	0.07 ± 0.02	0.02 ± 0.02	0.11 ± 0.02
C	0.23 ± 0.02	0.14 ± 0.02	0.16 ± 0.02	0.15 ± 0.02
D	0.05 ± 0.02	0.03 ± 0.02	0.01 ± 0.02	0.01 ± 0.02

Table 4.29 Changes in proton chemical shifts for A3 following dissolution of phenol derivatives.

In all cases the greatest shift occurred for the methylene protons α to the amine group (C hydrogens). Phenol caused the largest shift (0.23 ppm), with substituted phenols causing a shift of only *ca* 0.15 ppm. The proton shifts of the amine functionality did not correlate with facilitated fluxes or the pK_as of the substrate but in all cases an interaction between the amine functionality and the aromatic substrate appear likely from the chemical shift data. In view of the relatively small chemical shift changes, no attempt was made to vary the phenol : amine mol ratio and determine the stoichiometry of the reaction.

4.7 CONCLUSIONS TO TRANSPORT EXPERIMENTS INVOLVING AMINE FUNCTIONALISED POLY(ORGANOSILOXANE) SLMs

Batch runs using PDMS and amine functionalised poly(organosiloxane) SLMs were initially carried out with feed phases of aqueous phenol solutions of 15,000-35,000 ppm. These experiments demonstrated that phenol could be transported against a concentration gradient if a basic stripping phase is used. A 1.0M NaOH stripping phase is sufficiently basic such that over 99% of the phenol entering it is in the ionised form. Under these conditions a SLM consisting of pure PDMS can extract up to 65% of the initial phenol in the feed phase. For amine functionalised poly(organosiloxane) SLMs this value increases with increase in amine loading to a maximum of *ca* 95% (using A3) for initial phenol feed phase concentrations of 15,000-35,000 ppm. It has been shown experimentally that molecular phenol has a much greater permeability through PDMS than the phenate ion, and the difference in permeability increases with amine loading of the PDMS. Thus an increase in the phenol transport rate occurs with increased amine loading (see equation 1.1). Batch experiments gave no indication whether facilitated transport also occurred.

Continuous flow experiments were than carried out in order to elucidate the key features in the transport mechanism. These showed that facilitated transport occurs in some systems. Experiments using stripping phases consisting of 0.1M NaOH and distilled water enabled the facilitated fluxes for the transportation of phenol through the three amine-functionalised fluids to be determined. Facilitated fluxes increase with increase in amine loading. As found for conventional amine carriers[87-90], the facilitated flux is directly related to carrier concentration, and it also increases with increasing feed concentration until the saturation point is reached. Thereafter flux is independent of feed substrate concentration.

Both the amine functionalised poly(organosiloxane)s A1 and A2 SLMs have facilitated fluxes of *ca* 10 g/hour/m^{-2} at a 10,000 ppm phenol feed concentration. These

values are approximately the same as those for the TOA/sulphuric acid SLM[88]. A3 (30% amine loading) exhibits a facilitated flux of *ca* 36 g/hour/m^{-2} at 10,000 ppm phenol feed concentration. This is six times that found for the TOA/sulphuric acid SLM[88]. The overall phenol fluxes through A1-A3 were all much higher than those through a TOA/sulphuric acid SLM.

Substrates other than phenol were used to gain information about the transport mechanism. No facilitation effects were found for benzyl alcohol, indicating that for facilitation to occur with amine functionalised siloxanes an acidic substrate is needed. The facilitated fluxes of the phenol derivatives hydroquinone (pK_a 10.35) and methoxyphenol (pK_a 10.17) were similar to those of phenol at similar concentrations, so indicating that slight changes in the acidity and steric bulk of the substrate have little effect on the transport mechanism.

The generally low working lifetime of SLMs is one very important reason why SLM technology has not been used more frequently in industry, and one aim of this project was to determine whether replacement of conventional carrier/solvent systems by poly(organosiloxane)s leads to a improvement in this property. This project showed that the working lifetimes of amine functionalised poly(organosiloxane) SLMs are determined by the amine loading and the substrate being transported. The higher the amine loading and substrate flux the lower the stability of the SLM. The working lifetimes of the A1 and A2 SLMs for phenol are comparable with those of amine carrier[87-90] and solvent[80] systems involving flat sheet supports.

CHAPTER 5

ETHER FUNCTIONALISED POLY(ORGANOSILOXANE) SLMs

5.0 ETHER FUNCTIONALISED POLY(ORGANOSILOXANE) SLMs

INTRODUCTION

In this chapter the results of the transport experiments using ether functionalised poly(organosiloxane)s as integrated solvent/carrier SLM systems are discussed. The ether functional group was chosen in order that a functionalised poly(organosiloxane) with a polar but non-basic side arm could be compared with the amine functionalised poly(organosiloxane) SLMs. Although the ether side group can interact with phenol through H-bonding, this is likely to be a considerably weaker interaction than that in the amine/phenol system. It was hoped that comparing the results for these two types of functionalised poly(organosiloxane)s would reveal information on the importance of the strength of the carrier-substrate interaction in the facilitated transport mechanism operative in these systems.

Another reason for investigating ether functionalised poly(organosiloxane)s is so that comparisons could be made with the polyglycol SLM produced by Monsanto[98]. Ether functionalised poly(organosiloxane)s have a number of chemical and physical properties which should be beneficial compared to those of polyglycol in SLM based separations of phenol and analogous substrates (see section 1.7).

5.1 BATCH EXPERIMENTS WITH PHENOL AS THE TEST SUBSTRATE

5.1.1 BATCH EXPERIMENTS WITH AN 11% ETHER FUNCTIONALISED POLY(ORGANOSILOXANE)

The 11% ether functionalised poly(organosiloxane) was chosen as the liquid membrane material upon which all the primary investigations were carried out in order to determine the optimum conditions for batch studies.

The conditions which were varied and their effects assessed were:

i) The length of the batch run.

ii) The NaOH concentration in the stripping phase.

iii) The pH of the feed phase.

5.1.1.1 STEADY STATE WITH 11% ETHER FUNCTIONALISED POLY(ORGANOSILOXANE) SLMs

The time taken to reach steady was found as previously (section 4.1.2.1). This involved stopping a batch run at varying times and determining the concentration of phenol in the stripping phase. The feed phase initially contained 15,000 ppm of phenol and the stripping phase was 1M NaOH solution.

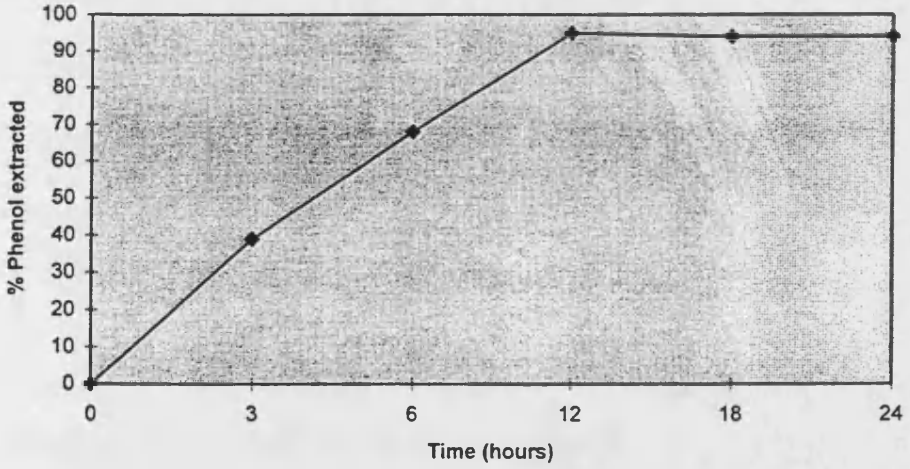


Figure 5.1 Percentage of phenol extraction as a function of time for the 11% ether functionalised poly(organosiloxane),E2.

After *ca* 12 hours the system had reached equilibrium and consequently all future batch runs were carried out over a 12 hour period. These results are very similar to those for the analogous amine functionalised poly(organosiloxane) SLMs system (see figure 4.1).

5.1.1.2 THE EFFECT OF NaOH CONCENTRATION IN THE STRIPPING PHASE ON THE TRANSPORT OF PHENOL

Batch runs were carried out using distilled water, 0.1M and 1M NaOH respectively as stripping phases. The percentages of phenol extracted into these stripping phases are shown in table 5.1.

Initial feed phase phenol conc. (ppm)	Distilled water stripping phase (% phenol)	0.1M NaOH stripping phase (% phenol)	1.0M NaOH stripping phase (% phenol)
15,000	49 ± 2	82 ± 2	92 ± 2
25,000	50 ± 2	70 ± 2	99 ± 2
35,000	49 ± 2	65 ± 2	98 ± 2

Table 5.1 Percentage of phenol extracted into stripping phases of differing pH.

When using distilled water as the stripping phase no significant pH gradient existed across the membrane once transportation has started, and as expected at equilibrium *ca* 50% of the phenol had been transferred into the stripping phase, in accord with Ficks first law.

If the results in table 5.1 are compared with those using amine containing poly(organosiloxane) SLMs (table 4.1) they show that E2 gives very similar results to A2. On using 1M NaOH as the stripping phase, phenol extraction was at *ca* 98% slightly higher than that found using membrane A2. This slightly higher extraction figure indicates that the phenate ion has a lower permeability, or that phenol has a higher permeability, through an ether functionalised poly(organosiloxane) compared with an amine functionalised poly(organosiloxane) of similar loading.

The pH of the 1.0M NaOH stripping phase at steady state was unchanged from the start at *ca* 13 whereas the pH of the 0.1M NaOH stripping phase had fallen to *ca* 10. Theses figures are similar to those obtained in studies using the analogous amine

functionalised (organosiloxane) SLMs i.e. NaOH is increasingly neutralised by phenol as noted for the amine functionalised SLMs, and hence the concentration of unionised phenol tends to equalise on both sides of the membrane, as shown by calculations in section 4.2.1.

5.1.1.3 EFFECT OF pH OF THE FEED SOLUTION ON THE TRANSPORT OF PHENOL

To investigate if the magnitude of the pH gradient across the membrane has any effect on the amount of phenol extracted, a series of runs were carried out using a feed phase solution consisting of 0.1M HCl (pH 1). The results were compared with analogous runs using distilled water (pH 5) as the feed phase.

Initial feed phase phenol conc. (ppm)	Distilled water feed phase (% phenol)	0.1M HCl Feed phase (% phenol)
15,000	92 ± 2	93 ± 2
25,000	99 ± 2	98 ± 2
35,000	98 ± 2	98 ± 2

Table 5.2 The percentage of phenol extraction using 0.1M HCl and distilled water as the feed phase.

It can be seen that lowering the pH of the feed has no effect on the percentage of phenol extracted using E2. A similar finding was noted for the amine functionalised poly(organosiloxane) A2 SLMs. Thus the pH gradient is important in keeping a concentration gradient of non-ionised phenol across the membrane, but increasing the pH gradient has little effect on the degree of extraction.

5.1.2 THE EFFECT OF ETHER CARRIER CONCENTRATION ON THE EXTRACTION OF PHENOL

The effect on phenol extraction of increasing the ether functional group loading has also been investigated, with the results summarised below in Table 5.3.

Initial feed phase phenol conc. (ppm)	PDMS (% phenol)	E1 (4% ether) (% phenol)	E2 (11% ether) (% phenol)	E3 (29% ether) (% phenol)
15,000	65 ± 2	83 ± 2	92 ± 2	FAILED
25,000	66 ± 2	86 ± 2	99 ± 2	FAILED
35,000	64 ± 2	84 ± 2	98 ± 2	FAILED

Table 5.3 Percentage of phenol extraction using different ether loadings.

No results was obtained for E3 SLMs as *ca* 50% of the siloxane fluid had leached from the pores of the support after 12 hours and the membrane failed. E1 and E2 SLMs permitted the transport of slightly higher quantities of phenol than the analogous SLMs A1 and A2 (see section 4.1.3), indicating that the permeabilities of phenol and/or the phenate ion are different in these two types of functionalised siloxane. Further speculation on these data is unjustified.

5.2 DYNAMIC CONTINUOUS FLOW EXPERIMENTS

Continuous flow experiments were carried out on ether functionalised poly(organosiloxane) SLMs in order to determine whether the ether group acts as a carrier in a facilitated transport mechanism, or whether it simply alters the solubility of phenol in the functionalised poly(organosiloxane).

5.2.1 CONTINUOUS FLOW EXPERIMENTS USING AN 11% ETHER FUNCTIONALISED POLY(ORGANOSILOXANE) SLM

The 11% functionalised ether poly(organosiloxane) E2 was also chosen as the liquid membrane material upon which all the primary investigations into the optimum conditions for continuous flow studies were carried out.

The conditions which were varied and their effects assessed were:

i) The phenol feed concentration.
ii) The NaOH concentration in the stripping phase.
iii) The pH of the feed phase.

5.2.1.1 THE EFFECT OF FEED PHENOL CONCENTRATION ON PHENOL FLUX

The first run carried out used a phenol feed phase concentration of 10,000 ppm and the stripping phase consisted of 0.1M NaOH. As can be seen from the data in figure 5.3, the concentration of phenol in the stripping phase increases rapidly over 1.5 hours and then levels off and reaches a steady state in *ca* 2.5 hours (see figure 5.2). This corresponds almost exactly with the results found for A2. Further runs were carried out under the same conditions with phenol feed phase concentrations ranging from 15,000 to 35,000 ppm. The results are summarised in table 5.4.

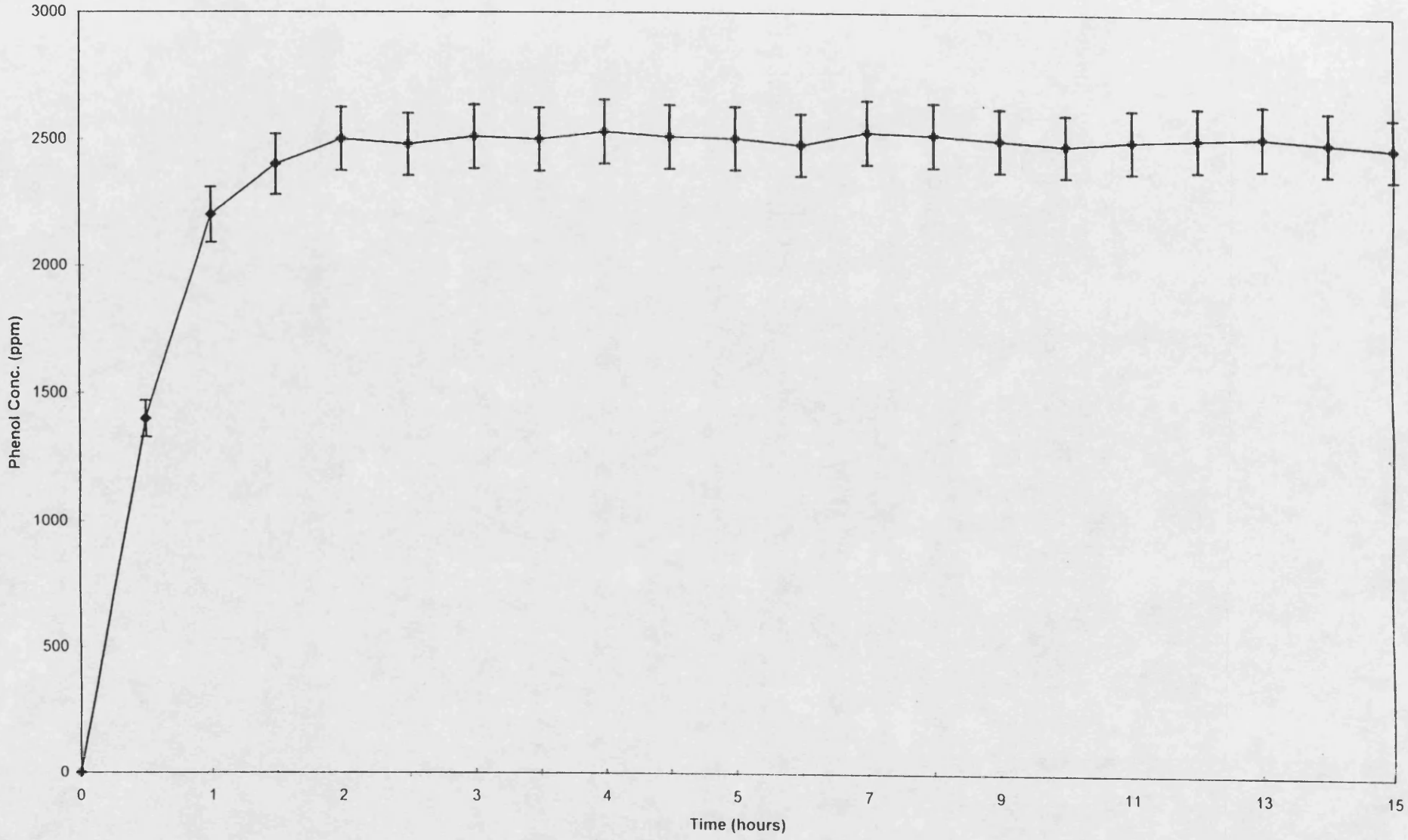


Figure 5.2 Concentration of phenol in the stripping phase against time.

Initial phenol feed phase conc. (ppm)	Phenol flux g/hour/m^{-2}
10,000	87 ± 5
15,000	121 ± 5
20,000	167 ± 5
25,000	243 ± 5
30,000	275 ± 5
35,000	302 ± 5

Table 5.4 Phenol fluxes for a range of phenol feed concentrations.

Figure 5.3 shows the results obtained for E2, A2 and PDMS membranes. Much greater fluxes were found using E2 than A2 at any given phenol concentration, and the flux difference increases at higher phenol feed concentrations. Thus at 35,000 ppm the phenol flux using E2 is almost twice that for A2.

5.2.1.2 THE EFFECT OF NaOH CONCENTRATION ON THE PHENOL FLUX

The batch experiments for both the ether and amine functionalised poly(organosiloxane)s indicate that a threshold concentration of NaOH exits, at which level the phenol exists entirely in the form of phenate ion in the stripping phase. The amine functionalised poly(organosiloxane) SLMs continuous flow experiments indicated that a stripping phase NaOH concentration of 0.1M was required to ensure this. To confirm that flux was independent of NaOH concentration above 0.1M, several runs were carried out using E2 with 0.2M NaOH as the stripping phase. The results are shown in table 5.5 and confirm that the phenol flux is not effected by doubling the NaOH concentration in the stripping phase. Consequently all other runs were carried out using a 0.1M NaOH stripping phase solution.

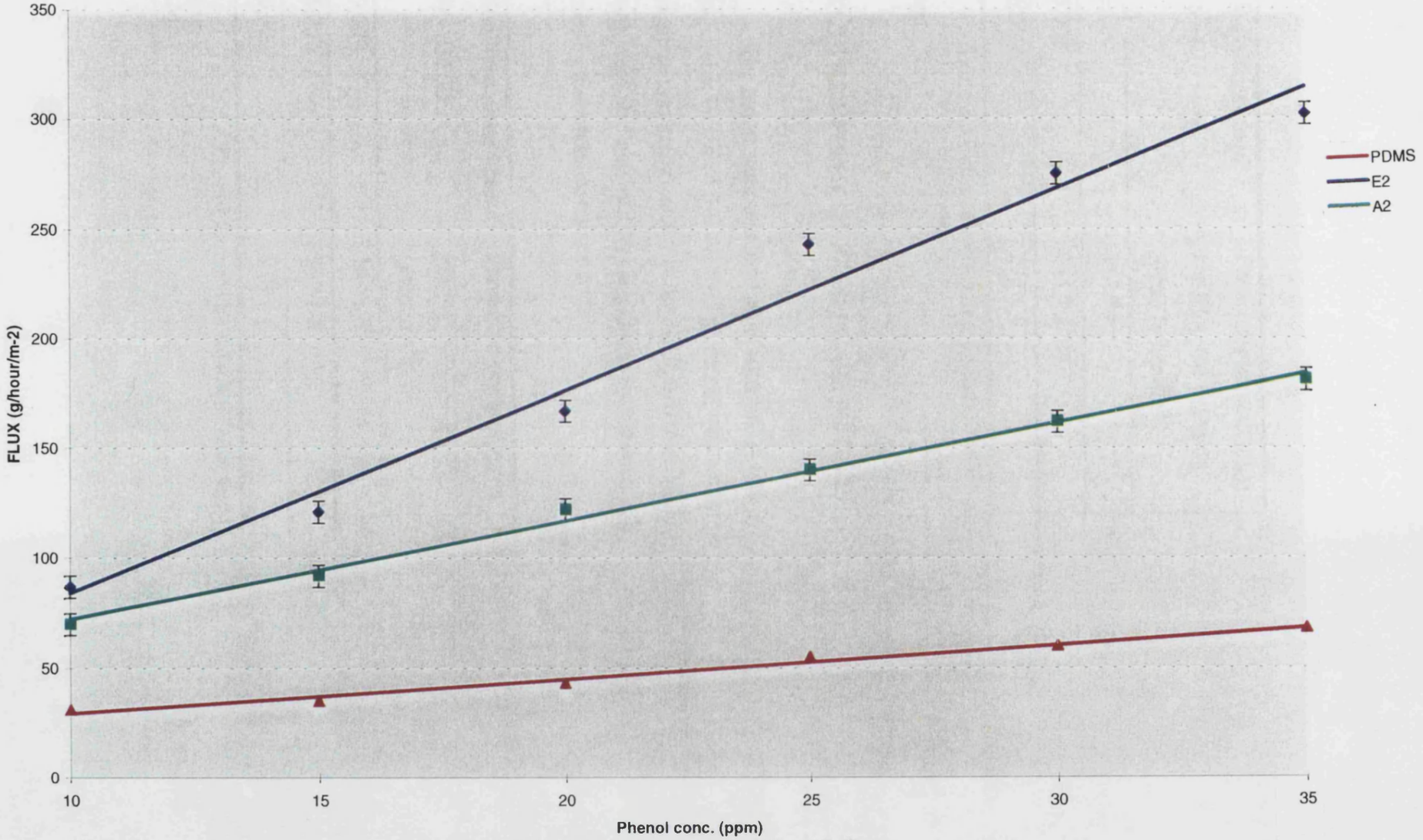


Figure 5.3 Phenol fluxes through E2, A2 and PDMS.

Initial phenol conc. (ppm)	Phenol fluxes with 0.1M NaOH as the stripping phase (g/hour/m^{-2})	Phenol fluxes with 0.2M NaOH as the stripping phase (g/hour/m^{-2})
20,000	167 ± 5	165 ± 5
25,000	243 ± 5	246 ± 5
30,000	275 ± 5	273 ± 5

Table 5.5 Phenol fluxes using different NaOH concentrations in the stripping phase.

5.2.1.3 THE EFFECT OF FEED PHASE pH ON PHENOL FLUXES

The amine functionalised poly(organosiloxane) SLMs continuous flow experiments indicated that the feed phase pH was not important as long as the pH of the feed phase was sufficiently low for the phenol to be in the non-ionised form. The same results were also obtained for the ether functionalised poly(organosiloxane) SLMs, as shown by the results in table 5.6

Initial feed phase phenol conc. (ppm)	Phenol flux with distilled water as the feed phase (g/hour/m^{-2})	Phenol flux with 0.1M HCl as the feed phase (g/hour/m^{-2})
20,000	167 ± 5	170 ± 5
25,000	243 ± 5	245 ± 5
30,000	275 ± 5	274 ± 5

Table 5.6 Phenol fluxes with distilled water and HCl as the feed phase using E2 SLMs.

5.2.2.THE EFFECT OF ETHER FUNCTIONAL GROUP LOADING ON PHENOL FLUX

The effect of changing the ether functional group loading was investigated by comparing the results obtained for E2 with those for E1 and E3 for transport experiments involving initial phenol concentrations in the range 10,000-35,000 ppm. The fluxes obtained for the various phenol feeds are shown in table 5.7.

Initial phenol conc. (ppm)	PDMS flux g/hour/m^{-2}	E1 (4% ether) flux g/hour/m^{-2}	E2 (11% ether) flux g/hour/m^{-2}	E3 (29% ether) flux g/hour/m^{-2}
10,000	31 ± 5	49 ± 5	87 ± 5	125 ± 5
15,000	35 ± 5	66 ± 5	121 ± 5	170 ± 5
20,000	43 ± 5	87 ± 5	167 ± 5	219 ± 5
25,000	55 ± 5	105 ± 5	243 ± 5	275 ± 5
30,000	60 ± 5	130 ± 5	275 ± 5	302 ± 5
35,000	68 ± 5	143 ± 5	302 ± 5	358 ± 5

Table 5.7 Phenol fluxes through each of three ether functionalised poly(organosiloxane) SLMs, E1-E3.

As can be seen from table 5.7 the flux increases with increase in the ether functional group loading. The fluxes for E3 are *ca* 5 times those through PDMS and *ca* 1.5 times those through A3. To determine whether the increase in phenol flux for the ether functionalised poly(organosiloxane) SLMs compared with the amine functionalised poly(organosiloxane) SLMs is due to the ether functionality acting as a more effective carrier, or simply due to solubility effects, the pH gradient must be reduced to zero and the facilitated flux determined.

5.2.3 THE TRANSPORT OF PHENOL WITH ZERO pH GRADIENT ACROSS THE SLM

Runs were carried out using membrane E1-E3 and a distilled water stripping phase so that no pH gradient exits across the membrane once transport of phenol starts. Experimental data on phenol fluxes were then subjected to the same treatment as that described in section 4.2.3, in order that the facilitated flux could be calculated. The results are summarised in table 5.8.

All the ether SLMs show facilitated flux effects. Unexpectedly the facilitated flux is essentially the same for the three membranes E1, E2 and E3. This observation has not been reported previously in the literature[29] as an increase in carrier concentration is expected to increase the facilitated flux. If a "jumping" mechanism is operative in all three of the ether functionalised poly(organosiloxane)s SLMs, this could generate the equivalent of "channels" from one side of the membrane to the other, then transport might occur at a similar rate in all the cases. Work carried out at the University of Bath[140] has shown that a "jumping" mechanism does indeed occur in the transport of lactic acid derivatives through functionalised poly(organosiloxane) SLMs. These studies also showed that there was a critical functional loading at which the "jumping" mechanism took over from the diffusion mechanism and that this occurred at considerably higher loading than 4%. Further investigation are needed into the transport mechanism occurring in ether functionalised poly(organosiloxane) SLMs before a convincing explanation for the observed trend can be given.

Polymer	Feed phase phenol conc. (ppm)	Unionised phenol conc. gradients with NaOH stripping phase (ppm) ΔC_{NaOH}	Unionised phenol conc. gradients with water stripping phase (ppm) ΔC_{water}	ΔC_{NaOH} /ΔC_{water}	Phenol flux (water stripping phase) g/hour/m^{-2}	Corrected phenol flux (water stripping phase) g/hour/m^{-2}	Phenol flux (0.1M NaOH stripping phase) g/hour/m^{-2}	Facilitated flux g/hour/m^{-2}
E1	10,000	10,000	9,180	1.089	31 ± 5	34 ± 5	49 ± 5	15 ± 10
E1	15,000	15,000	13,800	1.087	45 ± 5	49 ± 5	66 ± 5	17 ± 10
E1	20,000	20,000	18,500	1.081	57 ± 5	62 ± 5	57 ± 5	25 ± 10
E1	25,000	25,000	23,300	1.037	64 ± 5	69 ± 5	105 ± 5	36 ± 10
E1	30,000	30,000	27,650	1.085	89 ± 5	97 ± 5	130 ± 5	33 ± 10
E1	35,000	35,000	32,280	1.084	103 ± 5	112 ± 5	143 ± 5	31 ± 10
E2	10,000	10,000	8,200	1.219	68 ± 5	83 ± 5	87 ± 5	0 to 15
E2	15,000	15,000	12,700	1.181	87 ± 5	103 ± 5	121 ± 5	18 ± 5
E2	20,000	20,000	16,700	1.198	125 ± 5	150 ± 5	167 ± 5	17 ± 5
E2	25,000	25,000	20,400	1.225	174 ± 5	213 ± 5	243 ± 5	30 ± 5
E2	30,000	30,000	24,700	1.215	200 ± 5	243 ± 5	275 ± 5	32 ± 5
E2	35,000	35,000	29,000	1.207	226 ± 5	273 ± 5	302 ± 5	29 ± 5
E3	10,000	10,000	7,800	1.282	83 ± 5	106 ± 5	125 ± 5	19 ± 10
E3	15,000	15,000	11,800	1.271	121 ± 5	154 ± 5	170 ± 5	16 ± 10
E3	20,000	20,000	16,000	1.250	151 ± 5	189 ± 5	219 ± 5	30 ± 10
E3	25,000	25,000	20,000	1.250	189 ± 5	236 ± 5	275 ± 5	39 ± 10
E3	30,000	30,000	24,200	1.246	219 ± 5	272 ± 5	302 ± 5	30 ± 10
E3	35,000	35,000	28,200	1.241	257 ± 5	319 ± 5	358 ± 5	39 ± 10

Table 5.8 Facilitated fluxes at various phenol feed concentration for membranes E1-E3.

5.2.4 THE EFFECT OF STIRRING RATE ON PHENOL FLUX

One possible reason why phenol facilitated fluxes are independent of ether group loading could be that the boundary layer provides the limiting step. Experiments were carried out with changed stirring rates in order to test this possibility. The stripping phase used in all cases was 0.1M NaOH solution.

Phenol feed phase conc.(ppm)	Stir rate 500 rpm approx. (g/hour/m^{-2})	Stir rate1000 rpm approx. (g/hour/m^{-2})
15,000	120 ± 5	121 ± 5
20,000	170 ± 5	167 ± 5
25,000	240 ± 5	243 ± 5

Table 5.9 Phenol fluxes at different stirring rates.

The stirrers were unable to operate above 1000 rpm which set the top speed for the experiments, but the results in table 5.9, taken together with the fact that the overall phenol flux increases with increase in ether loading, indicate that it is extremely unlikely that transport through the boundary layer is the limiting rate determining step.

5.3 TRANSPORT OF PHENOL DERIVATIVES USING ETHER FUNCTIONALISED POLY(ORGANOSILOXANE) SLMs

Transport experiments were carried out in order to investigate the effect of changing substrate acidity on the facilitated flux. The substrates used were hydroquinone (pK_a 10.35), p-bromophenol (pK_a 9.18) and p-methoxyphenol (pK_a 10.17). These p-substituted phenol derivatives were chosen in order to minimise steric differences between them and phenol, so that valid comparisons could be made.

The facilitated fluxes for hydroquinone and p-methoxyphenol through amine functionalised poly(organosiloxane) SLMs (table 4.20 and 4.21) were slightly lower

than analogous data for phenol. This we believe is due to the higher pK_a of these two substrates compared to phenol. If this trend was repeated for an ether functionalised poly(organosiloxane) it would add extra support to this argument. The bromophenol facilitated fluxes with amine functionalised poly(organosiloxane) SLMs were very much larger than those of phenol. This is probably due to two effects; the very high solubility of p-bromophenol in PDMS, and its lower pK_a. So it was expected that ether functionalised poly(organosiloxane) SLMs would give similar results to those of amine functionalised poly(organosiloxane) SLMs.

5.3.1 TRANSPORT OF HYDROQUINONE AND p-METHOXYPHENOL

The experiments with hydroquinone (Hy) as the substrate were carried out with feed phase concentrations of hydroquinone ranging from 15,000 to 35,000 ppm. E2 was used as the ether functionalised poly(organsiloxane) in the SLMs.

Feed phase Hy conc. (ppm)	Unionised Hy conc. gradients with NaOH stripping phase (ppm) ΔC_{naOH}	Unionised Hy conc. gradients with water stripping phase (ppm) ΔC_{water}	ΔC_{NaOH} /ΔC_{water}	Hy flux (water stripping phase) g/hour/m^{-2}	Corrected Hy flux (water stripping phase) g/hour/m^{-2}	Hy flux (0.1M NaOH stripping phase) g/hour/m^{-2}	Facilitated flux g/hour/m^{-2}
15,000	15,000	14,950	1.005	Trace	Trace	15 ± 5	15 ± 10
20,000	20,000	19,950	1.003	Trace	Trace	17 ± 5	17 ± 10
25,000	25,000	24,940	1.002	Trace	Trace	23 ± 5	23 ± 10
30,000	30,000	29,940	1.002	Trace	Trace	24 ± 5	24 ± 10
35,000	35,000	34,940	1.002	Trace	Trace	27 ± 5	27 ± 10

Table 5.11 Hydroquinone (Hy) fluxes through an E2 SLM.

p-Methoxyphenol was used at a single feed phase concentration of 15,000 ppm, which is close to its maximum water solubility.

Polymer	Feed phase methoxy phenol conc. (ppm)	Unionised methoxy phenol conc. gradients with NaOH stripping phase (ppm) ΔC_{naOH}	Unionised methoxy phenol conc. gradients with water stripping phase (ppm) ΔC_{water}	ΔC_{NaOH} $/\Delta C_{water}$	Methoxy-phenol flux (water stripping phase) g/hour/m^2	Corrected methoxy-phenol flux (water stripping phase) g/hour/m^2	Methoxy-phenol flux (0.1M NaOH stripping phase) g/hour/m^2	Facilitated flux g/hour/m^2
E1	15,000	15,000	14,395	1.042	23 ± 5	24 ± 5	31 ± 5	0 to 17
E2	15,000	15,000	13,800	1.087	45 ± 5	49 ± 5	68 ± 5	19 ± 10
E3	15,000	15,000	14,440	1.116	60 ± 5	67 ± 5	83 ± 5	16 ± 10

Table 5.12 Methoxyphenol fluxes through E1-E3 SLMs.

As noted in table 5.11 and then shown in figure 5.4, hydroquinone facilitated fluxes are slightly lower than the analogous phenol facilitated fluxes but fall within experimental error. The same trend was found for amine functionalised poly(organosiloxane) SLMs (see section 4.3.1). Thus the results from both the ether- and amine-functionalised poly(organosiloxane) experiments indicate that a slight change in pK_a from phenol to hydroquinone may have an affect on the facilitated flux. The facilitated fluxes for methoxphenol are very similar to those of the analogous phenol runs so the change in pK_a from phenol to methoxyphenol is not significant.

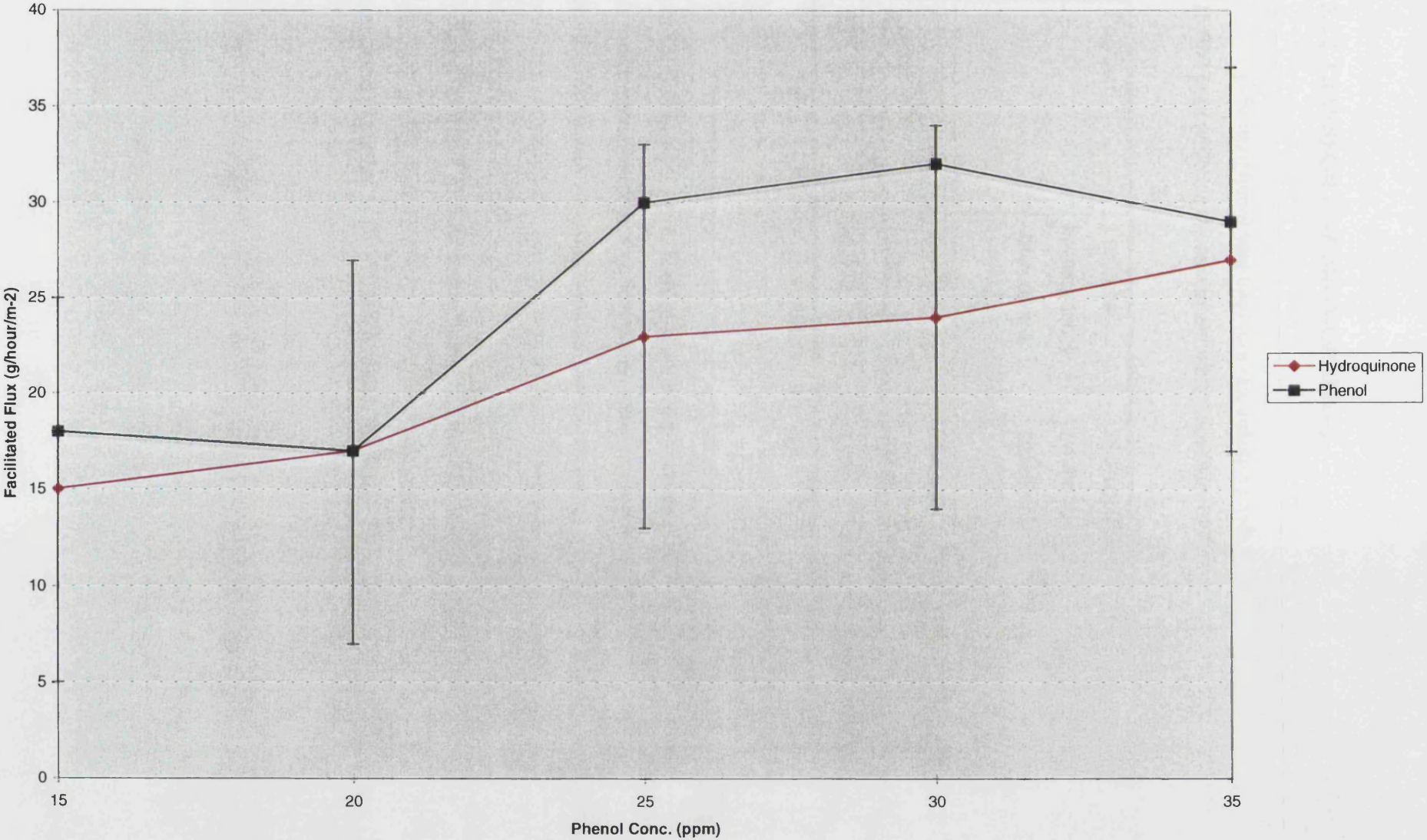


Figure 5.4 Hydroquinone and phenol fluxes through E2.

5.3.2 TRANSPORT OF BROMOPHENOL

p-Bromophenol was used as a test substrate with a feed phase concentration of 15,000 ppm which is the maximum water solubility of bromophenol.

Polymer	Feed phase bromophenol conc. (ppm).	Bromophenol flux (water stripping phase) g/hour/m^2	Bromophenol flux (0.1M stripping phase) g/hour/m^2
E1	15,000	208 ± 5	264 ± 5
E2	15,000	217 ± 5	358 ± 5
E3	15,000	220 ± 5	358 ± 5

Table 5.13 Bromophenol fluxes through E1-E3.

The bromophenol fluxes are all very large in comparison to the analogous phenol fluxes, with extractions of bromophenol being *ca* 6,000 ppm when using water as the stripping phase and *ca* 9,500 ppm when using 0.1M NaOH as the stripping phase. No facilitated flux was calculated for these systems, as the concentration gradient of unionised bromophenol across the membrane when using a 0.1M NaOH stripping phase is not known as a function of time. This was due to pH of the stripping phase being reduced to *ca* pH 11.5 so approximately 20% of the bromophenol in the stripping phase is present in the unionised form. The greater solubility of unionised bromophenol compared to phenol in PDMS is the reason for greater overall bromophenol fluxes.

5.3.3 BATCH RUNS ON PHENOL DERIVATIVES

In batch investigations phenol derivatives were used as the test substrate in order to determine if slight changes in the pK_a of the test substrate affected the percentage extraction of the compound. The feed phase concentration of each of the substrates initial was 15,000 ppm and the stripping phase was 1.0M NaOH.

Compound	PDMS (%)	E1 (4% ether) (%)	E2 (11% ether) (%)	E3 (29% ether) (%)
Phenol	65 ± 2	83 ± 2	92 ± 2	FAILED
Hydroquinone	<40	<40	<40	<40
Methoxyphenol	47 ± 2	60 ± 2	88 ± 2	94 ± 2
Bromophenol	80 ± 2	90 ± 2	FAILED	FAILED

Table 5.14 Percentage extraction of phenol derivatives at a feed phase concentration of 15,000 ppm.

The SLM containing E1 was the only one of the three SLMs which was stable for each of the substrates for the duration of the experiments. The percentage extraction of the substrates follows the order: bromophenol > phenol > methoxyphenol .> hydroquinone. This is same sequence as the overall fluxes in the continuous run experiments. The overall substrate fluxes are strongly influenced by the solubility of the unionised form of the substrate in PDMS, and it is apparent that percentage extraction of a substrate in a batch experiment is also determined by the same factor. The percentage extraction of each of the substrates through E1-E3 SLMs are very similar to those for through A1-A3 SLMs (see table 4.23).

5.4 TRANSPORT OF BENZYL ALCOHOL AND PHENOXYACETIC ACID

5.4.1 THE TRANSPORT OF BENZYL ALCOHOL

In order to investigate whether ether functionalised poly(organosiloxane) SLMs could transport a polar but non-acidic compound, transport studies were carried out using benzyl alcohol as the test substrate. The experiments were carried out under the same conditions as the phenol investigations. Benzyl alcohol feed concentrations ranged from 10,000 to 35,000 ppm.

Polymer	Feed phase benzyl alcohol conc. (ppm)	Fluxes g/hour/m^{-2} (Water stripping phase) A	Fluxes g/hour/m^{-2} (Water stripping phase) B	Difference in flux (A-B) g/hour/m^{-2}
E1	10,000	32 ± 5	27 ± 5	5 ± 10
E1	15,000	47 ± 5	43 ± 5	4 ± 10
E1	20,000	61 ± 5	57 ± 5	4 ± 10
E2	10,000	52 ± 5	46 ± 5	6 ± 10
E2	15,000	61 ± 5	67 ± 5	-6 ± 10
E2	20,000	85 ± 5	80 ± 5	5 ± 10
E2	25,000	110 ± 5	109 ± 5	1 ± 10
E2	30,000	137 ± 5	139 ± 5	-2 ± 10
E2	35,000	158 ± 5	160 ± 5	2 ± 10
E3	10,000	74 ± 5	59 ± 5	15 ± 10
E3	15,000	99 ± 5	93 ± 5	6 ± 10
E3	20,000	131 ± 5	118 ± 5	13 ± 10
E3	25,000	156 ± 5	147 ± 5	9 ± 10
E3	30,000	208 ± 5	196 ± 5	12 ± 10
E3	35,000	221 ± 5	208 ± 5	13 ± 10

Table 5.15 Benzyl alcohol fluxes for each of three ether functionalised poly(organosiloxane)s.

Both E1 and E2 show no facilitated flux, a similar result to that obtained result with the amine functionalised poly(organosiloxane)s (see section 4.4.1). The result for E3 indicates that it probably can facilitate the transport of benzyl alcohol with facilitated fluxes of the order of 12 g/hour/m^{-2} but the results for E3 are not completely conclusive and further work needs to be carried out on this system.

5.4.2 TRANSPORT OF PHENOXYACETIC ACID

Transport investigations were also carried out using phenoxyacetic acid (pK_a, 5.12) as substrate, in order to investigate the effect of using a relatively strong organic acid on flux. The feed phase concentration was 10,000 ppm and the stripping phase was 0.1M NaOH.

Polymer	E1 (4% ether)	E2 (11% ether)	E3 (29% ether)
Flux (g/hour/m^{-2})	4 ± 3	4 ± 3	6 ± 3

Table 5.16 Phenoxyacetic acid fluxes through E1-E3.

Table 5.16 shows the fluxes to be very low. This reflects the very low solubility of phenoxyacetic acid in ether functionalised poly(organosiloxane)s, and indicates that solubility is the major factor in determining the magnitude of the flux. These results are similar to those obtained for the amine functionalised poly(organosiloxane)s (see section 4.4.2), which also indicate the poor solubility of phenoxyacetic acid in PDMS.

5.5 STABILITY OF ETHER FUNCTIONALISED POLY(ORGANOSILOXANE) SLMs

As noted before the short working lifetime of SLMs is a very important factor which limits the application of SLM technology in industry. One important aspect of this study was to determine whether using functionalised poly(organosiloxane) polymers would produce SLMs of improved stability.

Runs were carried out using E1-E3 SLMs with an initial feed phase phenol concentration of 15,000 ppm and a stripping phase consisting of 0.1M NaOH. The results are show in figure 5.5. It was found that E1 SLM was still operating at optimum rate after 3 days, but as the ether loading increases the SLM stability decreases. Thus E2 is stable for *ca* 48 hours whereas E3 is stable only for *ca* 12 hours. Compared to the analogous amine functionalised poly(organosiloxane) SLMs (see section 4.5), E1 and E2 have comparable working lifetimes but E3 is less stable than A3. As noted before (see section 4.3) an inverse relationship exits between SLM stability and flux. This conforms with the observation that E3 has low stability as its overall phenol fluxes are considerably higher than those of A3.

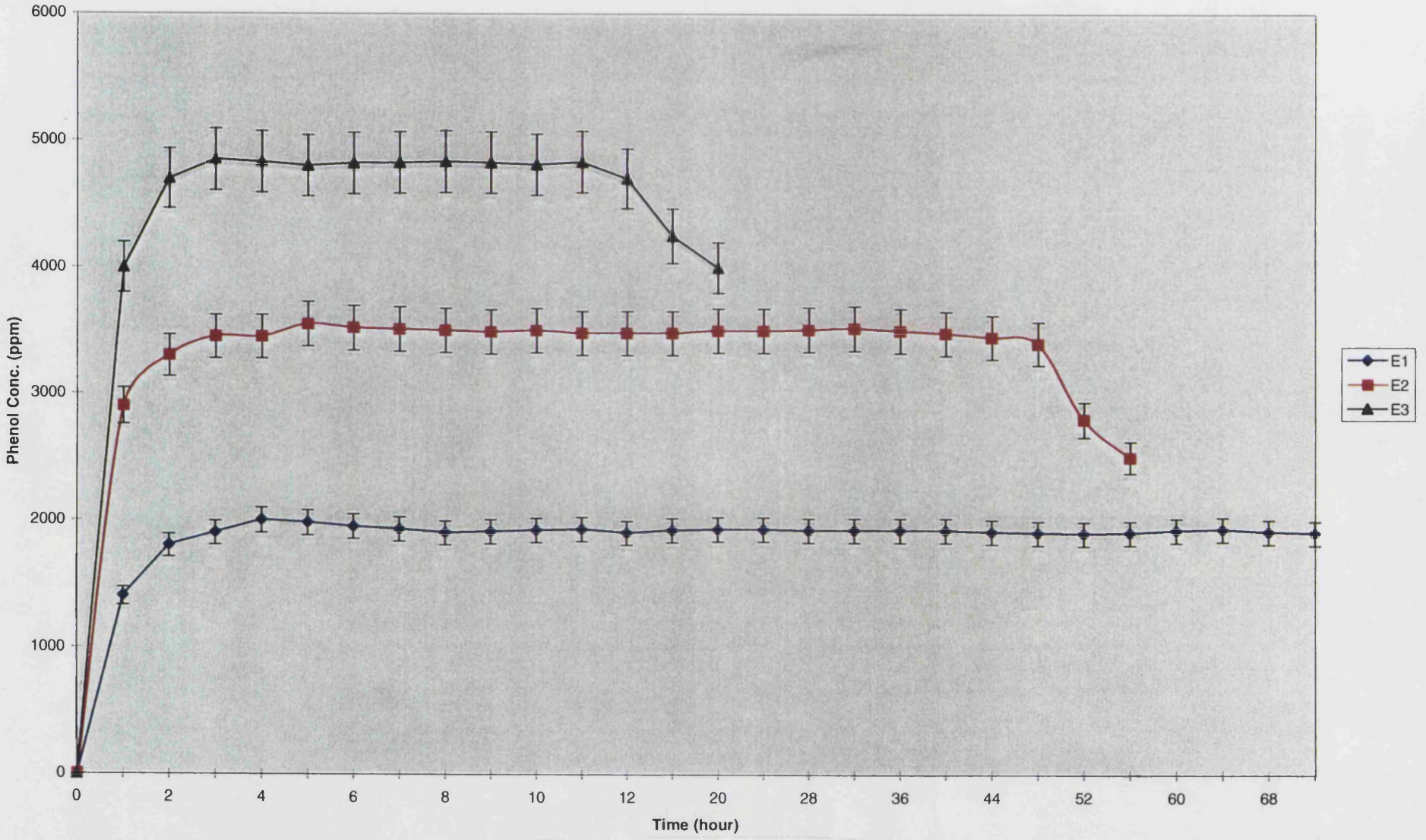


Figure 5.5 Working lifetime of E1-E3 SLMs.

5.6 SPECTROPHOTOMETRIC AND ^{1}H NMR INVESTIGATIONS OF THE H-BONDING BETWEEN PHENOL AND ETHER FUNCTIONALISED POLY(ORGANOSILOXANE)S

IR studies carried out at Monsanto[98] on the transport of p-nitrophenol through polyglycol confirmed that the ether links in the polyglycol backbone hydrogen-bond with the substituted phenol (see section 1.6.3.1). It was suggested that H-bonding is an important feature of the transport process[98]. Further evidence that ethers H-bond to phenols has been gained by solid state structural studies[96-97] (see section 1.6.3). In this project it has been noted that ether and amine functionalised poly(organosiloxane)s can facilitate the transport of phenol, but as there is no pervious experimental evidence for interactions in solution between phenol and ether functionalised poly(organosiloxane)s, IR and ^{1}H NMR studies were carried out using a typical ether functionalised poly(organosiloxane) and phenol in order to monitor any interactions, and to compare the results with those obtained at Monsanto[98] for polyglycol.

5.6.1 IR STUDIES OF THE INTERACTION OF PHENOL WITH ETHER FUNCTIONALISED POLY(ORGANOSILOXANE)S

Solid phenol was dissolved in the various ether functionalised poly(organosiloxane)s E1-E3 (*ca* 20% phenol wt/wt), and IR spectral measurements were recorded on a Nicolet 570P FTIR instrument using NaCl plates.

E1	E2	E3
3389 ± 4 cm^{-1}	3381 ± 4 cm^{-1}	3368 ± 4 cm^{-1}

Phenol (solid)	PDMS	C3 (30% butyl)	A3 (30% amine)
3327 ± 4 cm^{-1}	3382 ± 4 cm^{-1}	3383 ± 4 cm^{-1}	3330 ± 4 cm^{-1}

Table 5.17 Maxima of phenol O-H_{str} in a range of functionalised poly(organosiloxane)s.

The OH_{str} maxima of phenol dissolved in PDMS was observed at 3382 cm^{-1}. Inter and intramolecular H-bonding is possible and the value of 3382 cm^{-1} was taken as a "blank" against which others could be compared. The O-H maxima of phenol dissolved in E1 and E2 change little compared to that of phenol in PDMS, indicating that the ether functionality has little effect on the mode of H-bonding of phenol dissolved in these PDMS derivatives. The O-H maximum of phenol dissolved in E3 shifts *ca* 14 cm^{-1} compared to the blank, indicating that at high ether loadings the mode of H-bonding between phenol and the fluid polymer changes. For comparative purposes the IR spectra obtained by Monsanto[98] are shown in figure 1.12. The OH_{str} of p-nitrophenol (PNP) was observed at 3330 cm^{-1}. Infrared spectra were recorded using NaCl plates. Data are reported as peak maxima (ν_{max}) in wavenumbers (cm^{-1}).

In a 20% solution of PNP in polyglycol this absortption shifts by 140 cm^{-1} to 3190 cm^{-1}. This is a far greater shift than that found for phenol in E3. This may reflect the fact that PNP is more acidic (pK_a 5.12) than phenol, and that the whole backbone of polyglycol consists of ether segments, as opposed to a minor proportion as in the ether functionalised poly(organosiloxane)s.

5.6.2 ^{1}H NMR STUDIES ON THE INTERACTION OF PHENOL AND AN ETHER FUNCTIONALISED POLY(ORGANOSILOXANE)

The ^{1}H NMR spectrum of E3 saturated (20% wt/wt) with phenol was compared with the ^{1}H NMR spectrum of pure E3. Changes in proton chemical shift for the hydrogens of the ether functionality are noted in table 5.18. The proton shift of the hydroxyl group of phenol could not be determined accurately because of the broadness of the signal.

$O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3$

B A C

Hydrogens	E3 (29% ether) (ppm)	E3 + Phenol (ppm)	Difference (ppm)
A	3.82 ± 0.01	3.87 ± 0.01	0.05 ± 0.02
B	3.51 ± 0.01	3.57 ± 0.01	0.06 ± 0.02
C	1.21 ± 0.01	1.20 ± 0.01	0.01 ± 0.02

Table 5.18 Change in ^{1}H NMR chemical shifts of E3 on addition of phenol.

The shift in the protons A and B is only *ca* 0.05 ppm. This suggests that the interaction between the phenol and the ether functionality is probably weak. The maximum chemical shift for phenol/A3 was 0.23 ppm (see section 4.6.2), indicating a much stronger interaction, as expected on Lewis acid-Lewis base arguments. Due to time limitations more detailed ^{1}H NMR studies were not attempted.

5.7 CONCLUSIONS TO TRANSPORT EXPERIMENTS INVOLVING ETHER FUNCTIONALISED POLY(ORGANOSILOXANE) SLMs

Batch runs using ether functionalised poly(organosiloxane) SLMs were initially carried out with aqueous feed phases with phenol concentrations of 15,000-35,000 ppm. These experiments demonstrated that if 1.0M NaOH is used as the stripping phase an ether functionalised poly(organosiloxane) SLMs will transport phenol very effectively against a concentration gradient. Using a 1.0M NaOH stripping phase 98 ± 2 % of the phenol was extracted at steady state for E2 (11 mol %) SLM with an initial feed phase phenol concentration of 35,000 ppm. This value is slightly greater than that for the analogous amine functionalised poly(organosiloxane). This probably reflects a greater permeability of phenol through an ether functionalised poly(organosiloxane) compared with an amine functionalised poly(organosiloxane) of the same loading (see equation 1.1).

Continuous flow experiments were than carried out in order to investigate the transport mechanism. Experiments using stripping phases consisting of 0.1M NaOH and distilled water respectively enabled the facilitated fluxes for transportation of phenol through three ether functionalised fluids to be determined. It was found that facilitated fluxes did not increase with increase in ether loading, as noted for conventional SLMs. The facilitated fluxes through E1-E3 were *ca* 25 ± 10 g/hour/m^{-2}. The reason for this behaviour is not clear and further investigations are need.

Substrates other than phenol were used to gain further information about factors affecting the transport mechanism. The facilitated fluxes of the phenol derivatives hydroquinone (pK_a 10.35) and methoxyphenol (pK_a 10.17) were similar to those of phenol at similar concentrations, so indicating that slight changes in the acidity and steric bulk of the substrate have little effect on the transport mechanism. The ether functionality is unable to interact with phenol via an acid/base interaction but may depend on a polar interaction between functionality and substrate to effect the

transportation of phenol. Benzyl alcohol was used as a test substrate to determine whether a less acidic substrate than phenol was similarly transported. E1 and E2 showed no facilitation for benzyl alcohol but E3 showed a small facilitated flux indicating that a high loaded ether functionalised poly(organosiloxane) can be used to transport polar but non-acidic substrates. The working lifetime of the ether functionalised poly(organosiloxane) SLMs is determined by the ether loading and substrate flux, with lower stability with higher flux and higher ether loadings. E1 and E2 have similar working lifetime to A1 and A2 but the stability of E3 is less than that of A3, possibly due to the considerably higher overall phenol fluxes in this membrane.

CHAPTER 6

ESTER AND BUTYL FUNCTIONALISED POLY(ORGANOSILOXANE) SLMs

6.0 BUTYL AND ESTER FUNCTIONALISED POLY(ORGANOSILOXANE) FLUIDS IN SLM TRANSPORT EXPERIMENTS

6.1 PHENOL TRANSPORT THROUGH ESTER FUNCTIONALISED POLY(ORGANOSILOXANE) SLMs

INTRODUCTION

It has been shown previously that both amine and ether functionalised poly(organosiloxane) SLMs can be used for the facilitated transport of phenol, but the interactions between substrate and fluid are different in the two cases. The results described in chapter 5 show that although the ether functionalised poly(organosiloxane) interact only weakly with phenol, the interaction is sufficient to allow facilitated transport of phenol to occur. Esters are more polar than ethers hence they should interact more strongly than ethers with phenol[142,143]. This stronger interaction might result in increased facilitation.

Fluid D1 (28% ester loading) was used in the form of a SLM in combination with aqueous phenol solutions as the feed phase. Stripping phases used were 0.1M NaOH and distilled water, so that any facilitated flux could be determined. The results were calculated as previously, and are summarised in table 6.1.

Feed phase phenol conc. (ppm)	Unionised phenol conc. gradients with NaOH stripping phase (ppm) ΔC_{NaOH}	Unionised phenol conc. gradients with water stripping phase (ppm) ΔC_{water}	ΔC_{NaOH} /ΔC_{water}	Phenol flux (water stripping phase) g/hour/m^{-2}	Corrected phenol flux (water stripping phase) g/hour/m^{-2}	Phenol flux (0.1M NaOH stripping phase) g/hour/m^{-2}	Facilitated flux g/hour/m^{-2}
10,000	10,000	7,900	1.266	79	100	94	0 to 4
15,000	15,000	11,900	1.260	117	147	136	0 to 1
20,000	20,000	15,800	1.266	159	201	211	0 to20
25,000	25,000	20,800	1.263	196	250	260	0 to 20
30,000	30,000	23,700	1.266	238	301	302	0 to 11

Table 6.1 Facilitated phenol fluxes through D1 SLM.

As can be see from table 6.1, no facilitated phenol fluxes were achieved using D1. The reason for lack of facilitation may lie in investigations carried out by Bennett[144] *et al* on the separation of phenol using crosslinked ester functionalised poly(organosiloxane) pervaporation membranes. The phenol permeability through the ester functionalised poly(organosiloxane) membrane films was *ca* 3.5 times higher than through PDMS due to hydrogen bonding interactions between phenol and the ester functionality. Hydrogen bonding between water and the ester groups also enhance the water permeability through the same membrane by a factor of 4.5. The results from the studies by Bennett[144] *et al* are summarised in table 6.2.

Functional group	Chemical structure	loading %	Phenol permeability ($m^2s^{-1} \times 10^{-11}$)	Water permeability ($m^2s^{-1} \times 10^{-11}$)	Separation factor
PDMS		0	2.15	0.46	17.7
Acetate	$CH_2CO_2CH_3$	10	2.75	0.76	13.8
		20	7.58	2.11	13.1
Di-acetate	$CH(CO_2CH_3)_2$	20	3.18	0.73	16.5
Ether	$CH_2OC_2H_5$	10	3.07	0.41	27.6
		20	4.48	0.56	29.0
Amine	$CH_2N(CH_3)_2$	20	5.28	0.58	29.8

Table 6.2 Phenol and water permeability's through functional poly(organosiloxane) membrane films.

It was suggested[144] that the hydrogen bonding between ester groups and water molecules is particularly effective, as water is small and angular so that each end of a water molecule may hydrogen bond to one of the two oxygen atoms in the ester group, as depicted in figure 6.1, which explains the higher increase in flux for water as compared to phenol.

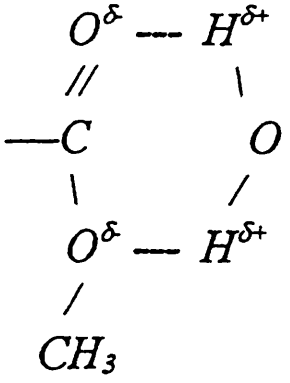


Figure 6.1 Hydrogen bonding of water and an ester functionality.

This competition between water molecules, present in large excess, and phenol, for the H-bonding sites of the ester group could be the reason no facilitation occurred.

6.2 PHENOL TRANSPORT THROUGH BUTYL FUNCTIONALISED POLY(ORGANOSILOXANE) SLMs

INTRODUCTION

Butyl functionalised poly(organosiloxane)s were used as SLMs to examine the effect of increasing the non-polar organic content of the poly(organosiloxane) on the transportation of phenol. The increased organic content should increase the solubility of phenol in the polymer, which in turn will affect the phenol flux. The two butyl functionalised poly(organosiloxane)s used were C1 and C2 which have butyl functional group loadings of 4% and 11% respectively. The stripping phases used were 0.1M NaOH and distilled water respectively so any facilitated flux could be determined. The results are summarised in table 6.3 and show that there is no facilitation effect.

These results are in accord with results on the other poly(organosiloxane) SLMs in that the overall phenol flux increases with the addition of organic functionality, but they are not as large as the phenol fluxes through ether and amine functionalised poly(organosiloxane)s.

Polymer	Feed phase phenol conc. (ppm)	Unionised phenol conc. gradients with NaOH stripping phase (ppm) ΔC_{NaOH}	Unionised phenol conc. gradients with water stripping phase (ppm) ΔC_{water}	ΔC_{NaOH} $/\Delta C_{water}$	Phenol flux (water stripping phase) g/hour/m^{-2}	Corrected phenol flux (water stripping phase) g/hour/m^{-2}	Phenol flux (0.1M NaOH stripping phase) g/hour/m^{-2}	Facilitated flux g/hour/m^{-2}
C1	10,000	10,000	9,400	1.064	23	24	23	0 to 9
C1	15,000	15,000	14,100	1.064	33	35	37	0 to 12
C1	20,000	20,000	19,000	1.052	38	40	43	0 to 13
C1	25,000	25,000	23,800	1.051	45	45	51	0 to 14
C1	30,000	30,000	28,400	1.056	59	62	64	0 to 12
C1	35,000	35,000	33,100	1.057	72	76	77	0 to 11
C2	10,000	10,000	9,100	1.099	35	38	34	0 to 6
C2	15,000	15,000	13,200	1.083	43	50	53	0 to 13
C2	20,000	20,000	18,200	1.099	68	75	79	0 to 14
C2	25,000	25,000	22,700	1.101	87	96	104	0 to 15
C2	30,000	30,000	27,350	1.096	100	122	132	0 to10
C2	35,000	35,000	31,900	1.097	117	129	137	0 to 18

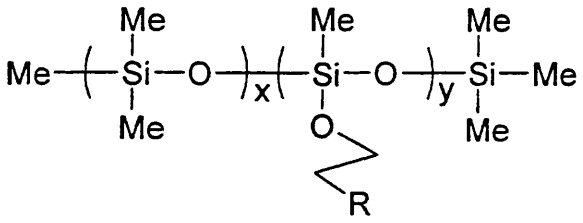
Table 6.3 Phenol fluxes through C1 and C2 SLMs.

CHAPTER 7

CONCLUSIONS AND FURTHER WORK

7.0 CONCLUSIONS AND FURTHER WORK

In this project a new general method for the synthesis of functionalised poly(organosiloxane)s has been developed. In this procedure functionalised poly(organosiloxane)s were synthesised in *ca* 90% yields by a hydrogen elimination reaction between a dimethylsiloxane-methylhydrosiloxane co-polymer and a primary alcohol in the presence of a platinum catalyst. Four classes of functionalised poly(organosiloxane)s fluids were synthesised containing amine, ether, ester or methyl functionality each with loadings of *ca* 4, 11, and 30 mol %. These functionalised poly(organosiloxane) were all stable for more than year, and were used successfully as supported liquid membranes.



R = CH_2NMe_2, OCH_2CH_3 , CH_2CH_3, $(CH_2)_3CO_2Et$

Of the four classes of functionalised poly(organosiloxane) produced only those containing amine and ether functionalities could transport phenol through a facilitated transport mechanism. The phenol facilitated flux through the amine functionalised poly(organosiloxane) SLMs increased with increase in amine loading but the phenol facilitated flux through ether functionalised poly(organosiloxane) is independent of ether loading over the range 4-29 mol %. A possible reason for this behaviour may originate from a change in the main transport mechanism, with the latter exhibiting a "jumping" process. In order to confirm a "jumping" mechanism, diffusion coefficients need to be calculated at various SLM thickness so that an average diffusion coefficient can be found for the process. This diffusion coefficient can than be compared to the diffusion coefficient obtained when phenol is being transported by normal diffusion of

the carrier/phenol complex. If the diffusion coefficients for the two systems are dissimilar than a jumping mechanism is probably in operation. Ensuring that phenol is transported only by diffusion of the carrier/phenol complex could be difficult without changing the system completely. One possible way would be to dissolve in PDMS the ether CH_3-CH_2-O-CH_2-CH_2-O-CH_3 which is chemically similar to the ether functional group and use this within the SLM. If a "jumping" mechanism is in operation calculations by Yahaya[140] indicate that a critical functional group loading exits below which level no facilitated transport will take place. Experiments should be carried out with ether group loading between 0.5 and 3.5% to find this critical functional group loading. If no critical loadings exits then a "jumping" mechanism is unlikely.

In this project the transport mechanism was investigate by using phenol derivatives. The results from these investigations demonstrated that slight changes in pK_a of the substrate have little effect on facilitated flux. Further investigations are needed to determine at what point pK_a becomes important. Non-aromatic water soluble alcohols such as glycerol (pK_a 14.15) and glycol (pK_a 14.22) could be used as substrates. However these compounds are non-aromatic uv-vis spectroscopy cannot easily be used directly to estimate them. Instead these alcohols could be coupled to dyes and then detected by uv-vis spectroscopy or directly by HPLC using a RI detector. As amines and ethers can be used as carriers in SLMs for the extraction of very different substrate types such as metals cations, inorganic anions and penicillin (see section 1.3), investigations with ether- and amine-functionalised poly(organosiloxane)s SLMs could be extended to these class of substrates.

As noted above the short working lifetime of SLMs is a very important factor which limits the application of SLM technology in industry. One important aspect of this study was to determine whether functionalised poly(organosiloxane) polymers could be used to produce SLMs of improved stability. The functionalised poly(organosiloxane) SLMs examined in this project were found to be have similar stabilities to those of conventional SLMs. One possible why of improving stability would be to increase the viscosity of the functionalised poly(organosiloxane) from *ca* 10

cpu as used in this project. This could be easily achieved by increasing the crosslinking. Increased viscosity would however reduce substrate permeability and hence the overall flux. One of the most successful method reported in the literature for improving the working lifetimes of SLMs has been the use of a thin stabilisation polymer layer attached to the surface of the SLM which allows the substrate through but prevents loss from the SLM. This could be tried for these functionalised poly(organosiloxane) SLMs using one of the stabilisation polymers PVC[145], polyamide[146] and poly(ether ketone)[147]which have been used in other systems. Another possible method of improving the working lifetimes of functionalised poly(organosiloxane) SLMs would be to chemically attach the functionalised poly(organosiloxane) to the support so preventing any loss from the SLM. A new support would be needed which has hydroxy groups on its surface such as cellulose[148] or glass. This would permit a condensation reaction with silanol terminated functionalised poly(organosiloxane)s. Such chemical adaptability is unique in the liquid membrane technology

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